

# CHARACTERIZATION AND LABORATORY SYNTHESIS OF COMMERCIAL DENTAL CERAMICS

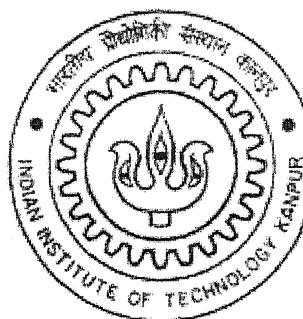
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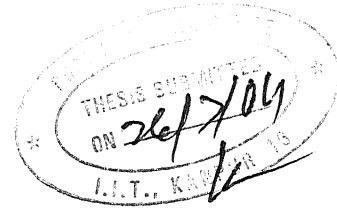
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JULY 2004



## CERTIFICATE

This is to certify that the work contained in the thesis entitled **“Characterization and laboratory synthesis of commercial dental ceramic”** by Mr. Vijay Kumar Tiwary has been carried out under my guidance and this work has not been submitted elsewhere for a degree.

(Dr. R. K. Ray)

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## **Abstract**

Dental ceramic technology has become one of the fastest growing areas of dental materials research and development since dental ceramics are considered to produce aesthetically the most pleasing result. Their colour, translucency and vitality cannot as yet be matched by any other material except other ceramics. The present study stresses on the characterization of three commercially available dental ceramics namely wash opaque (WO 3000), dentine (EN1, A3 3053) and enamel (EN2 3072) and a dental alloy having the trade name Bellabond N (BBN 81006). The present study also includes laboratory synthesis of these ceramics and their characterization. All the three received powders were found to have  $\text{SiO}_2$  as the major constituent present. Wash opaque powder was found to have a crystalline nature whereas dentine and enamel were non-crystalline. Leucite was the main crystalline phase present in wash opaque. The as received dental alloy was found to be a Ni-Cr based alloy.

Various experimental techniques such as optical microscopy, SEM/EDS analysis, TG/DTA analysis, XRD and chemical analysis were used for the purpose of characterization. The results obtained from the present work have been critically analysed and discussed and suitable and relevant conclusions were drawn therefrom. Finally, an attempt has been made to compare the laboratory synthesized materials with the materials that are commercially available.

## Chapter 1

### Introduction

Ceramics were the most sophisticated materials of the stone age more than 10,000 years ago, and they have retained their importance in human societies ever since. Most ceramic materials are characterized by their refractory nature, hardness, susceptibility to brittle fracture and chemical inertness. For dental applications, a ceramic should have hardness similar to that of enamel to minimize the wear of resulting ceramic restorations and to reduce the wear damage that can be produced on enamel by the ceramic restoration. The susceptibility to brittle fracture is a drawback, particularly when flaws and tensile stresses coexist in the same region of ceramics restoration. Chemical inertness is an important characteristic because it ensures that the surface of dental restorations does not release potentially harmful elements, and it reduces the risk of surface roughening and an increased susceptibility to bacterial adhesion over time. Two other important attributes of dental ceramics are their potential for matching the appearance of natural teeth and their insulating properties (low thermal conductivity, low thermal diffusivity and low electrical conductivity). Because the metal atoms transfer their outermost electrons to the nonmetallic atoms and thereby stabilize their highly mobile electrons, ceramics are excellent thermal and electrical insulators (1).

Notwithstanding the many advances made in the field of composites and glass-ionomers, a ceramic material known as porcelain holds a special place in dentistry because it is still considered to produce aesthetically the most pleasing result (2).

As people in modern times retain their teeth for much longer than in the past, the need for aesthetically acceptable restorations is continuing to increase. This is reflected in the growing use by dentists of restorative procedures using ceramics (2). Traditionally, dental ceramic materials are used in the construction of artificial teeth, dentures, crowns and bridges. But the past two decades have seen the development of shoulder porcelains for butt joint porcelain margins on porcelain fused to metal (PFM) crowns and all-ceramic inlay and crown material including high-leucite porcelain, shrink free core ceramic, injection-molded core ceramic, castable ceramic, computer-aided design and computer-aided machinable (CAD-CAM) ceramics, and high strength glass-infiltrated alumina core ceramic. Most of these

materials can be formed into inlays, onlays, veneers and crowns and they can be resin-bonded to tooth structure. The future of dental ceramics is bright because the increased demand for tooth-coloured restorations will lead to an increased demand for ceramic-based and polymer-based restorations in preference to the use of amalgam and traditional cast metals (1).

The present work has been undertaken to characterize three commercially available dental porcelains, namely wash opaque (WO 3000), dentine (EN1, A3 3053), and enamel (EN2 3072) and a dental alloy having the trade name Bellabond N (BBN 81006). The study also includes laboratory synthesis of these ceramics by reverse engineering followed by their characterization and comparison with similar existing materials.

In this thesis, Chapter 2 provides a brief introduction to the different types of dental porcelain and alloy, their properties and composition. Chapter 3 describes the experimental procedures that were used for laboratory synthesis of dental ceramics by reverse engineering and their characterization. It also includes characterization of the three as received dental ceramics and a dental alloy. Chapters 4 & 5 include the experimental results and discussions respectively. The conclusion arising out of the present work have been included in Chapter 6.

## Chapter 2

# Background

### 2.1 Dental porcelain

Conventional dental porcelain is a vitreous ceramic based on a silica ( $\text{SiO}_2$ ) network and potash feldspar ( $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ ) or soda feldspar ( $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ ) or both. Pigments, opacifiers, and glasses are added to control the fusion temperature, sintering temperature, thermal contraction coefficient and solubility. The feldspars used for dental porcelain are relatively pure and colourless. Thus pigments must be added to produce the hues of natural teeth or the colour appearance of tooth-coloured restorative materials that may exist in adjacent teeth.

Silica can exist in four different forms: crystalline quartz, crystalline cristoballite, crystalline trydymite and noncrystalline fused silica. Fused silica is a high melting material whose high melting temperature is attributed to the three-dimensional network of covalent bonds between silica tetrahedral, which are the basic structural units of the glass network. Fluxes (low-fusing glasses) are often included to reduce sintering temperature of the porcelain powder particles at low enough temperatures so that the alloy to which it is fired does not melt or sustain sag (flexural creep) deformation.

The sintering temperature of crystalline silica is too high for use in veneering aesthetic layers onto dental casting alloys. At such temperatures the alloys would melt. In addition, the thermal contraction coefficient of crystalline silica is too low for these alloys [1]. Bonds between the silica tetrahedral can be broken by the addition of alkali metal ions such as sodium, potassium and calcium. These ions are associated with the oxygen atoms at the corners of the tetrahedral units and interrupt the oxygen–silicon bonds. As a result, the three dimensional silica network contains many linear chains of silica tetrahedral that are able to move more easily at lower temperatures than the atoms that are locked into the three dimensional structure of silica tetrahedral. This ease of movements is responsible for the increased fluidity (decreased viscosity), lower softening temperature, and increased thermal expansion conferred by glass modifiers. Too high a modifier concentration however, reduces the chemical durability (resistance to attack by water, acids and alkalis) of the glass. In addition, if too many tetrahedra are disrupted, the glass may crystallize

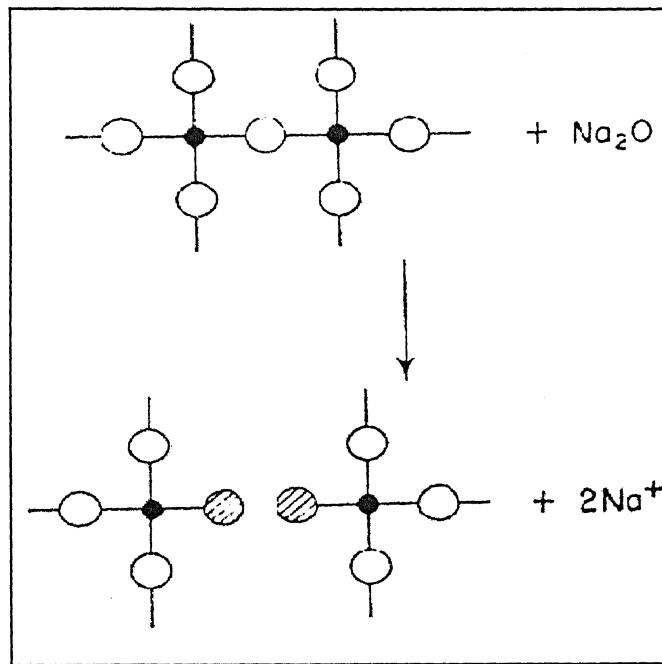
(devitrify) during porcelain firing operations. Hence, a balance between a suitable melting range and good chemical durability must be maintained [2, 3].

In addition to glass modifiers and fluxes (low fusing glasses) dental porcelain may also consist of several other oxides. Boric oxides ( $B_2O_3$ ) can behave as a glass modifier, that is, it decreases the viscosity, lowers the softening temperature and forms its own glass network. Because boric oxide forms a separate lattice interspersed with the silica lattice, it still interrupts the more rigid silica network and lowers the softening point of the glass. The role of alumina ( $Al_2O_3$ ) in glass formation is complicated. Alumina cannot be considered a true glass former by itself because of the dimensions of the ion and the oxygen: aluminum ratio. Nevertheless, it can take part in the glass network to alter the softening point and viscosity [4].

Pigmenting oxides are added to obtain the various shades needed to simulate natural teeth. These colouring pigments are produced by fusing metallic oxides together with fine glass and feldspar and then regrinding to a powder. These powders are blended with the unpigmented powdered frit to provide the proper hue and croma. Examples of metallic oxides and their respective colour contributions to porcelain include iron or nickel oxide (brown); copper oxide (green); titanium oxide (yellowish brown); manganese oxide (lavender); and cobalt oxide (blue) [1].

The porcelain powder used by the dental technician is not a simple mixture of the oxides mentioned. These powders have already been fired once. The manufacturer mixes the various oxides in appropriate ratio and fuses them, followed by fritting and crushing to a powder with a suitable size range of particles [5].

Dental restorations such as crown, bridges and the like are typically made of a metallic or porcelain core framework with one or more porcelain layers coated thereon. The porcelain layers provide the strength; wear resistance and favourable aesthetics to the dental restorations. In porcelain fused to metal restorations (PFM), it is important that the firing temperature of the porcelain be at least 100°C below the solidus temperature of the



**Fig. 2.1:** Reaction between sodium oxide and silica tetrahedral.

alloy used in the metal framework and that the coefficient of thermal expansion of the porcelain (in the range of room temperature to 450°C) be only very slightly less than that of the metal framework so that no stress cracks are produced in the porcelain during firing and cooling down. Ceramic cores are advantageous in the fabrication of dental restorations because concerns regarding effective concealment of the metal colour do not exist. Similar to metal cores, when a ceramic core is used, only porcelain applied to the ceramic framework must possess a coefficient of thermal expansion that is slightly less than that of the ceramic to prevent failure in the porcelain due to stresses caused by thermal expansion mismatch [1].

According to US PATENT 4879136 and US PATENT 5591030 the metallic substructure is coated with three different layers of porcelain namely opaque wash, dentine and enamel [6, 7].

**Opaque wash** is the first layer of multilayered porcelain-metal restorations. The function of this layer is to mask the colour of metallic substructure or core and develop a good bond with the core. The composition of opaque wash consists of glass forming and glass modifying oxides. Besides that some opacifying oxides such as  $ZrO_2$ ,  $TiO_2$  or  $SnO_2$  is added to obtain opacity [6].

**Dentine** and **enamel** are second and third layer of porcelain. Dentine is applied on top of opaque layer whereas enamel is applied on top of dentine. For dentine and enamel layers, the use of additional opacifying oxides such as  $TiO_2$  or  $SnO_2$  is not needed because of their high opacifying effect [6]. In place of these opacifying oxides some pigments are used which may be vanadates, manganates, chromates or transition metal oxides. The purpose of using pigments is to simulate the colour of metal-ceramic restoration with that of natural teeth [8, 9].

If desired, fluorescing agents such as cerium oxide, terbium oxide, yttrium oxide, and the like or other conventional additives can also be incorporated into the porcelain to simulate the natural dentition [6, 10].

## 2.2 Classification of dental porcelain

One of the most serious drawbacks of the early dental porcelains was their lack of strength and toughness, which seriously limited their use. As early as 1903, Land [5] described, in an issue of dental cosmos, how to make the porcelain crowns, but came up against the problem that the crowns would break too easily. Similarly, Pincus [5] described the concept of the ceramic veneer in an article in the Californian Dental Association Journal of 1938, but was also frustrated by the lack of strength of the porcelains available at the time. By that time, for reasons of aesthetics, the porcelain used contained little or no Kaolin.

In order to overcome the problem of lack of strength and toughness of dental porcelains, there are two possible solutions to the problem. One solution is to provide the dental porcelain with support from a stronger substructure. The other option is to produce ceramics, which are stronger and tougher. In this context, it is possible to consider dental ceramics to fall into three categories, based on the nature of the supporting structure:

- a) Reinforced ceramic core systems
- b) Resin-bonded ceramics
- c) Metal-ceramics

In each case the philosophy is to provide a high strength supporting structure for the ceramic providing the aesthetic finish. Obviously, ideal ceramic would have both the strength and the aesthetics to perform both functions. In case of reinforced ceramic core systems, the support for the aesthetic ceramic is provided by another ceramic material, which has the necessary high strength and toughness but may lack the desired aesthetics.

In contrast, in the case of resin-bonded ceramic, the support of the ceramic is provided by the tooth structure itself, by bonding the aesthetic ceramic directly to the enamel and dentine. In this instance the ceramic provides the necessary aesthetics and the strength is provided by the ability to bond to the tooth tissues. This approach only becomes possible with the advent of enamel and dentine bonding procedures. A combination of aesthetics and high strength would be ideal, as this removes the high reliance on the bond and also provides the opportunity to develop resin-bonded ceramic bridges.

In the case of metal-ceramic systems, a strong and tough metal supports the aesthetic ceramic.

### 2.2.1 Reinforced ceramic core systems

The early work by Land *et al* [5] had shown that one of the problems with the all-ceramic anterior crown was that the porcelain would fracture from the fit surface outwards. Some improvements in the strength of porcelain was achieved by the introduction of vacuum firing furnaces which helped to minimize porosity and raised the flexural strength of the porcelain from 20-30 MPa to approximately 50-60 MPa. However, this did not prove to be adequate and thus the search was on for a core material that would provide the necessary strength and toughness to prevent fracture arising from the cracks propagating from the frit surface of the crown. Since ceramics tend to fail at the same critical strain of  $\sim 0.1\%$ , one means of achieving increased fracture strength is to increase the elastic modulus of the material. If, at the same time, the propagation of cracks is made more difficult, such that a greater strain can be supported, a higher strength ceramic will result (Fig. 2.2). The flexural strengths of a number of ceramics are given in Table 2.1. As the tensile strength is a difficult property to measure (giving a wide degree of scatter in the data), it is common practice to determine the flexural strength.

**Table 2.1:** Typical strength values for high strength ceramics

Type of ceramic	Flexural strength (MPa)
Hot pressed silicon nitride	800-900
Hot pressed silicon carbide	400-750
Partially stabilized zirconia	640
Alumina 98% pure	420-520

Although silicon carbides and nitrides are attractive from the viewpoint of strength, they are not suitable because of the difficulties associated with the manufacture of individual crowns, the colour differences and the mismatch of the coefficient of thermal expansion.

In the mid-1960's, McLean and Hughes [5] developed a core material based on the reinforcement of a feldspathic glass with alumina, commonly referred to as the alumina-reinforced porcelain jacket crown. Since then, other systems have been developed. In the 1980's the glass-infiltrated high strength ceramic cores were developed (In-ceram, Vita Zahnfabrik, Bad Sackingen, Germany) and in the 1990's the all-alumina

core made its first appearance (Techceram, Techceram Ltd, Procera All Ceram, Nobel Biocare).

### 2.2.1.1 Alumina-reinforced porcelain jacket crown (PJC)

Based on a survey in 1994, metal-ceramic crowns and bridges were used for approximately 90% of all fixed restorations. However, recent developments in ceramic products with improved fracture resistance and excellent aesthetic capability have led to a slight increase in the use of all ceramic products. PJC's have been in widespread use since the beginning of the twentieth century. The ceramics employed in the conventional PJC were high fusing feldspathic porcelain. In the case of alumina-reinforced feldspathic core, introduced by Hughes and McLean [5] in the early 1960s, a feldspathic glass containing 40-50% alumina is used (Fig. 2.3). The alumina particles are stronger than glass, hence more effective at preventing crack propagation than quartz and act as crack stoppers (Fig. 2.4). The flexural strength of feldspathic porcelain is at best some 60 MPa but this is raised to 120-150 MPa for the aluminous core porcelains.

In the construction of a crown, the opaque shade is made with aluminous core porcelain (Fig. 2.5). It is still necessary to use the weaker dentine and enamel shades of feldspathic porcelains because it is not possible to produce aluminous porcelains with the required translucency; the alumina causes the porcelain to appear dull and opaque.

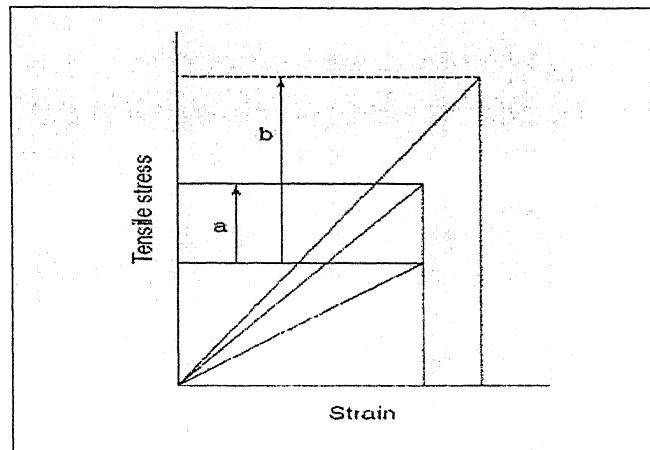
The alumina-reinforced PJC's are generally regarded as providing slightly better aesthetics for anterior teeth than metal-ceramic crowns that employ a metal coping. However, the strength of the core porcelain used for PJC's is inadequate to warrant the use of these restorations for posterior teeth. Thus, the newer high-strength ceramics are preferred for the production of PJC's [5, 11].

### 2.2.1.2 Glass infiltrated high strength ceramic core systems

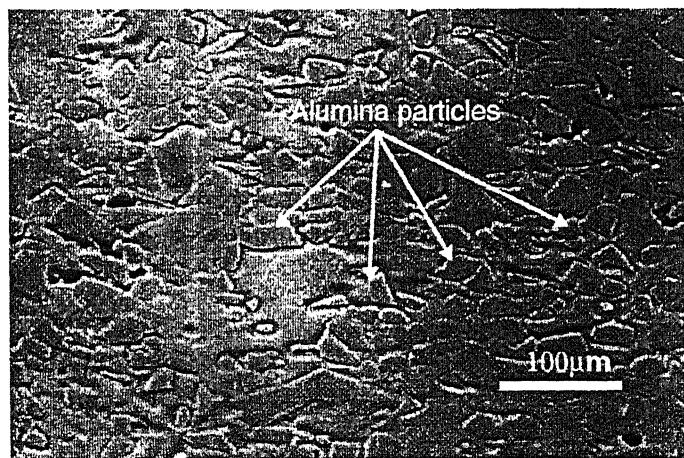
The addition of alumina to the feldspathic glass during the prefiring process limits the amount of alumina that can be incorporated to about 40-50 volume percent. An alternative approach has been adopted in a new system called In-Ceram (Vita). This core material has an alumina content of ~85%.

A ceramic core is formed onto the refractory die from fine slurry of alumina powder by a process known as slip casting. After the die has dried, it is sintered for 10 hrs at 1120°C. The melting temperature of alumina is too high to produce full densification of

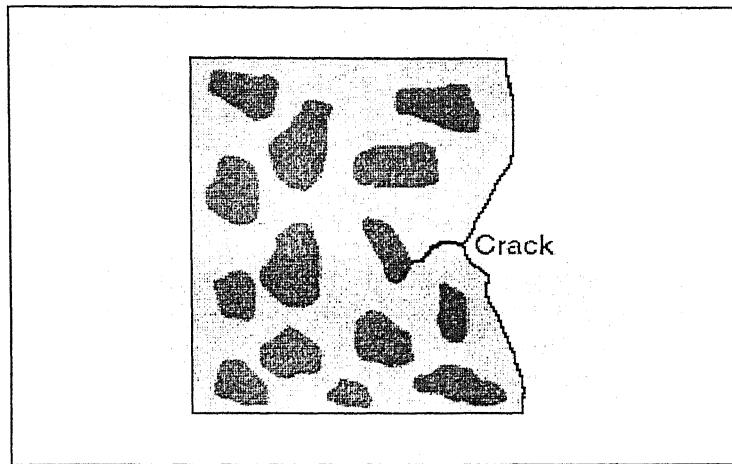
the powder by liquid phase sintering, and solid phase sintering alone occurs. Consequently, the coping thus created is only just held together at the contact points between the alumina particles, and a porous structure is the result. The strength of this porous core is only about 6-10 MPa. The porous structure is then infiltrated with a lanthanum glass, which has a low viscosity when fired at 1100°C for 4-6 hours. The molten glass is able to penetrate into the pores, producing a dense ceramic. The aesthetics



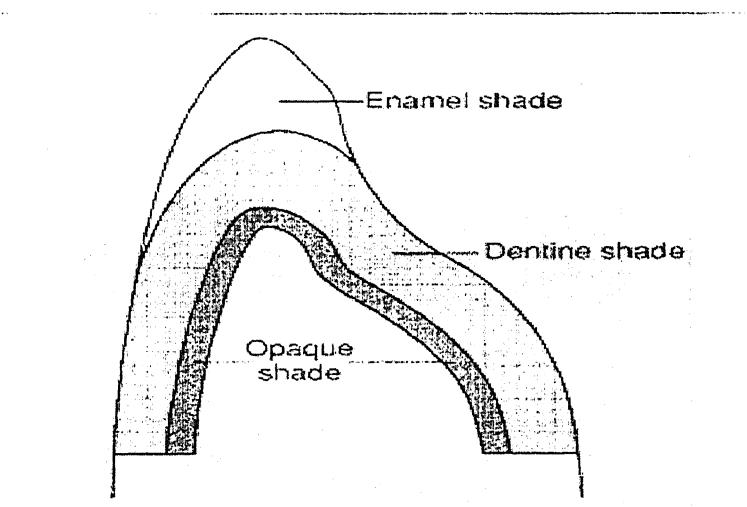
**Fig. 2.2:** Improvements in the strength of ceramics by (a) raising the elastic modulus and (b) increasing the resistance to crack propagation.



**Fig. 2.3:** SEM of an alumina reinforced core material showing the alumina particles embedded in a glassy matrix composed of feldspar.



**Fig. 2.4:** Alumina particles acting as crack stoppers.



**Fig. 2.5:** Porcelain build-up for a jacket crown.

and functional forms are then achieved by the use of conventional feldspathic dental ceramics.

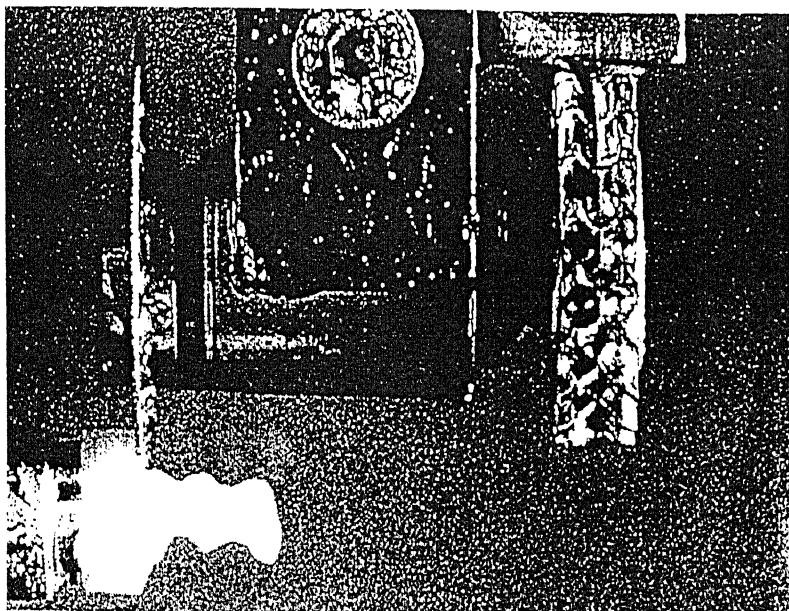
A similar approach has been adopted with spinel ( $MgAl_2O_4$ ) or zirconia replacing the alumina. The In-Ceram-Spinel offers superior aesthetics over the In-Ceram-Alumina at a slightly reduced flexural strength (~350 MPa) and is recommended for inlays. The In-Ceram-Zirconia is based on the In-Ceram-Alumina, but with the addition of 33 weights percent zirconia it produces a ceramic core with strength of about 700 MPa

An alternative route to the slip-casting route is now available for the CAD-CAM production route using either the CERAC system from Siemens or the Celay systems from Vident. The In-Ceram-Spinel/ Alumina/ Zirconia blocks from which the restorations are machined are produced by dry pressing the powder such that the open pore structure is denser and more homogeneous, leading to a yet higher flexural strength after glass infiltration [5, 12].

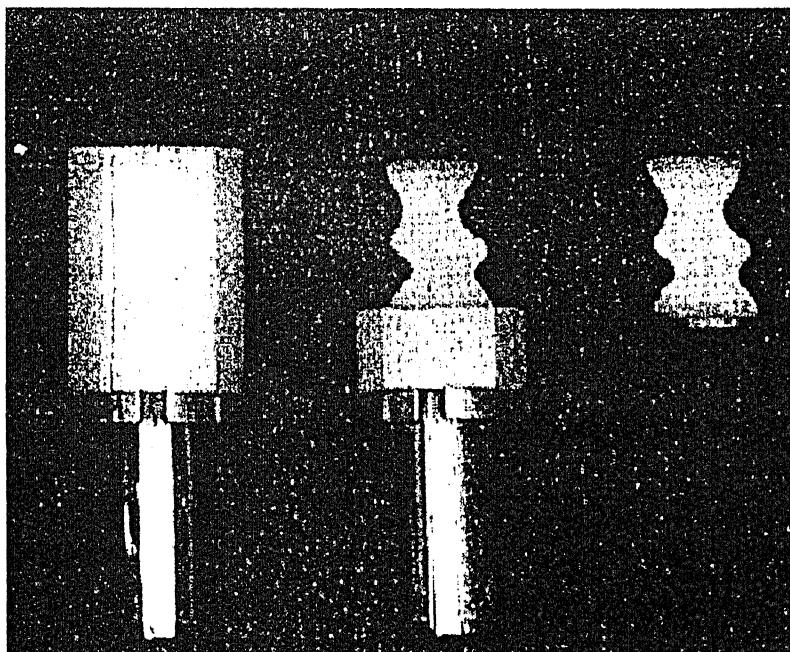
### 2.2.1.3 CAD-CAM ceramics

For the Cerec CAD-CAM system the internal surfaces of inlays, onlays or crowns are ground with diamond disks or other instruments to the dimensions obtained from a scanned image of the preparation. The external surface must be ground manually although some recent CAD-CAM systems are capable of grinding to the external surface as well. Fig. 2.6 shows the milling operation within a Cerec CAD-CAM unit. The ceramic block is being ground by a diamond-coated disk whose translation movements are guided by computer-controlled signals. A Cerec CAD-CAM ceramic block is shown in Fig. 2.7 before milling, at an intermediate milling stage, and after completion of the milling operation for an inlay.

These ceramics are supplied as small blocks that can be ground into inlays and veneers in a computer driven CAD-CAM system. Vita blocks MKII are feldspathic porcelains that are used in the same way as in Dicor MGC (machinable glass- ceramics). The disadvantages of CAD-CAM restorations include the need for costly equipment, the lack of computer-controlled processing support for occlusal adjustment, and the technique-sensitive nature of surface imaging that is required for the prepared teeth. Advantages include negligible porosity levels in the CAD-CAM core ceramics, the freedom from making an impression, reduced assistant time associated with impression



**Fig. 2.6:** Milling operation on a CAD-CAM ceramic block by a diamond –coated disk within the Cerec CAM station.



**Fig. 2.7:** CAD-CAM ceramic blocks before milling (left), at an intermediate stage of milling (Center), and after milling and removal of the inlay from the mounting stub (right) procedures, the need for only a single appointment (with the Cerec system), and good patient acceptance.

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#### 2.2.1.4 Pure alumina cores

It would seem a natural extension from the alumina-reinforced core systems to consider the possibility of a pure alumina core. There are at least two systems on the market that offer pure alumina cores, The Procera All Ceram (Nobel Biocare AB, Gutenberg, Sweden) and the Techceram system (Techceram Ltd, Shipley, UK). The potential advantages are increased strength and superior translucency compared with the glass-infiltrated core materials.

Production of the Procera All Ceram core involves producing a die from the impression, digitizing the geometry of the desired coping using specially designed computer software and transferring this information down a modem to a laboratory in Stockholm. This is all done by a designated dental laboratory that is a member of the Procera Network. The coping is produced by a special process, which involves sintering 99.5% pure alumina at 1600-1700°C such that it is fully densified. The coping is then returned to the dental laboratory for building in the crown's aesthetics using compatible feldspathic glasses. Turnaround time is approximately 24 hours. The flexural strength of the  $\text{Al}_2\text{O}_3$  core materials is in the region of 700 MPa, and thus similar to that achieved with the In-Ceram Zirconia.

The Techceram system uses quite a different approach. In this system the impression can be sent to Techceram Limited, who will produce a special die onto which the alumina core is deposited using a thermal gun-spray technique. This process produces an alumina core with a density of 80-90%, which is subsequently sintered at 1170°C to achieve optimum strength and translucency. The alumina coping is then returned to the

dental laboratory, where the ceramist will develop the final contour and aesthetics using conventional feldspathic glasses.

One drawback with all the high strength core systems described above is that none of them is amenable to acid etching to produce a micromechanically retentive surface, although some bonding with the cementing medium will arise owing to the roughness of the surface from processing. Since the fit surface is made of alumina rather than silica, no coupling agents are available that can effectively bond the core to resins. Without an effective coupling agent or an ideal micromechanically retentive surface, these systems cannot be resin-bonded to the tooth tissues and will not derive the added benefit associated with resin-bonded ceramic restorations [5].

### **2.2.2 Resin bonded ceramics**

One way in which the traditional approach of cemented restorations is being challenged is the development of new adhesive techniques. These have extended the use of ceramics to areas not previously thought possible. The combination of adhesion to enamel, dentine and ceramic and improved strength characteristics of the ceramics has produced restorations with excellent mechanical integrity. In fact, the adhesive bond has the effect of eliminating the internal surface flaws and thus reduces the potential for fracture. This has led to a growth in the use of ceramics for crowns, veneers and inlays.

The concept of using ceramics as veneers is not new, and can be traced back to Dr. Charles Pincus of Beverly Hills [5], who constructed porcelain veneers for actors in Hollywood. The porcelain veneers were baked on platinum foil and retained on the teeth by denture powder. However, the veneers often broke because the thin porcelain was brittle and they were frequently removed from the teeth. The acrylic resin was introduced in 1937; he switched to this material for the production of veneers for the acting profession. This eventually developed into the use of composite veneers, and ceramics were not used for a long time.

The re-emergence of all-ceramic veneers can be traced back to the early 1980s. At that time Dr. Horn [5] in America fabricated veneers on a foil backing and discovered that the fitting surface could be etched with hydrofluoric acid, thus improving the micromechanical retention. Using the phosphoric acid-etch technique on enamel he was able to bond the ceramic veneers permanently to the teeth with a resin-based composite. Bonding to ceramic has since been improved by the additional use of a silane-coupling agent.

Ceramic veneers are considered superior to composites because of their superior aesthetics, colour stability, surface finish, abrasion resistance and tissue compatibility. They are also chemically very stable and have a coefficient of expansion similar to that of enamel. The finishing of porcelain veneers is more difficult than that of composites due to their high hardness. The thin-feathered margins are more easily damaged than the margins of crowns, both in the laboratory and in the surgery. The ceramic veneers have the distinct advantages over crowns that improved aesthetics can be achieved with minimal tooth reduction, and the palatal surface of the tooth is unchanged so the incisal guidance is maintained.

Since then, there has been a major development of new ceramics suitable for use as resin-bonded all-ceramic restorations. The new materials have allowed the extension of the use of all-ceramic restorations from veneers to anterior and posterior crowns and inlays. The materials available for resin-bonded ceramic restoration are in essence varieties of a special group of ceramics known as glass ceramics. The various dental glass ceramics that have been developed for resin-bonded ceramic restorations are mainly Leucite-reinforced feldspar glass ceramic, Lithium disilicate and Apatite glass ceramics and fluoromica glass ceramics (Dicor).

### 2.2.2.1 Leucite reinforced feldspar glass ceramics

The ceramic used in the original experiments of Horn *et al* [5] was a leucite ( $KAlSi_2O_6$ ) – containing feldspathic glass, which he used in the construction of metal-ceramic restorations. This ceramic was optimized with regard to being able to bond to the metal surface. The ceramics used now for resin-bonded ceramic restorations are a modified version of the ceramic used by Horn *et al* [5]. They differ from the ceramic used in metal-ceramic primarily in that the composition and microstructure have been changed in order to produce the best leucite crystalline phase distribution from the point of view of strength, as compatibility with metal framework is no longer a consideration. This is by careful control of the composition and the ceraming heat treatment.

Whereas the leucite-containing ceramics used in metal-ceramic restorations have a flexural strength of the order of 30-40 MPa, the leucite-reinforced glass ceramics have flexural strengths of up to 120 MPa. A typical example of the structure of leucite – reinforced ceramic is shown in Fig.2.8.

### 2.2.2.2 Lithium disilicate and Apatite glass ceramics

In order to be able to extend the use of resin-bonded ceramic restorations and possibly use them for bridge construction, a glass ceramic based on a  $\text{SiO}_2\text{-LiO}_2$  system has been developed (Empress II, Ivoclar Vivadent, Schaan, Liechtenstein).

The crystalline phase ( $\text{Li}_2\text{Si}_2\text{O}_5$ ) makes up some 70% of the volume of the glass ceramics. Lithium disilicate has an unusual microstructure in that it consists of many small inter-locking plate-like crystals that are randomly oriented (Fig.2.9). This is ideal from the point of view of strength because the needle-like crystals cause cracks to deflect, branch or blunt; thus, the propagation of cracks through this material is arrested by the lithium disilicate crystals, providing a substantial increase in the flexural strength.

A second crystalline phase, consisting of a lithium orthophosphate ( $\text{Li}_3\text{PO}_4$ ) of a much lower volume, is also present.

The mechanical properties of this glass ceramics are far superior to that of the leucite glass ceramics, with a flexural strength in the region of 350-450 MPa and fracture toughness approximately three times that of the leucite glass ceramics. The high strength of lithium disilicate glass ceramics creates the possibility of not only producing anterior and posterior crowns, but also all-ceramic bridges.

Glass ceramics is claimed to be highly translucent due to the optical compatibility between the glassy matrix and the crystalline phase, which minimizes internal scattering of the light as it passes through the material.

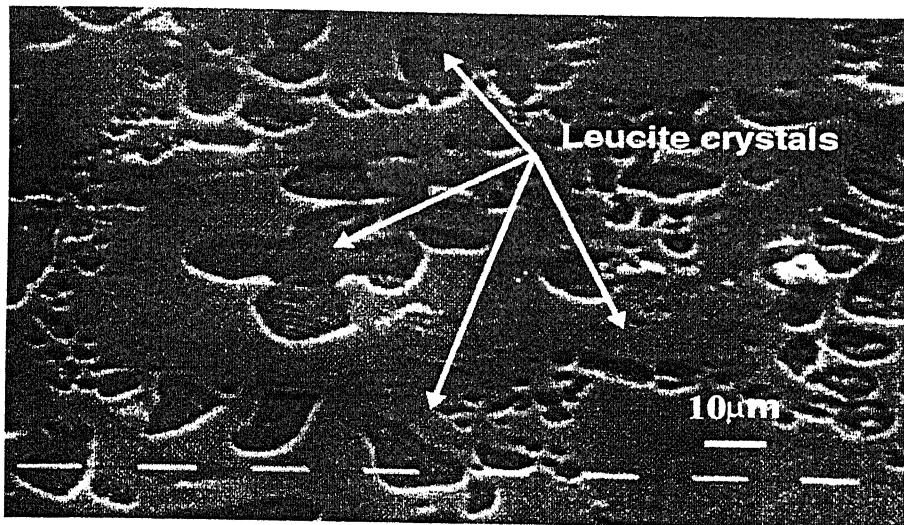


Fig. 2.8: SEM of the structure of a leucite-reinforced ceramics

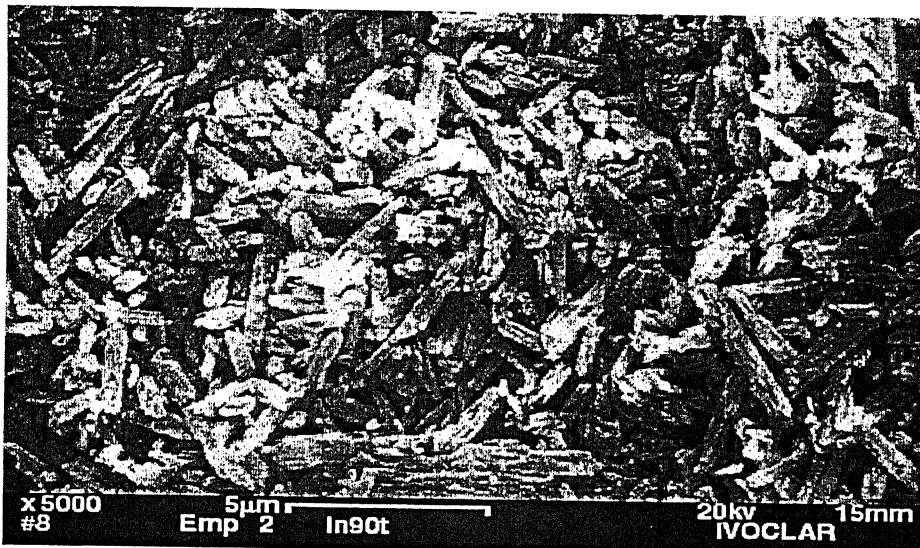


Fig. 2.9: SEM of the microstructure of a lithium disilicate glass ceramics, showing the interlocking needle -like crystals.

For the alumina based core systems as described earlier it is possible to use feldspathic glasses to provide the aesthetic surface layer, as their coefficients of expansion are closely matched at  $\sim 7\text{-}8 \text{ ppm}/^\circ\text{C}$ . For the leucite glass ceramics the layering ceramic is identical to the core ceramic and so a mismatch in coefficient of expansion does not arise. However, for the lithium disilicate glass ceramic the coefficient of thermal expansion is greater than  $10 \text{ ppm}/^\circ\text{C}$  and consequently a new compatible layering ceramic had to be developed. This new layering ceramic is an apatite glass ceramic. The crystalline phase formed on creaming is a hydroxy-apatite ( $\text{Ca}_{10}(\text{PO}_4)_6\cdot2\text{OH}$ ), which is the same basic constituent from which enamel is made. Thus, it represents a material that, at least in composition, is the closest match to enamel that has been achieved so far [5,13].

### 2.2.2.3 Fluoromica glass ceramics (e.g. Dicor)

Fluoromicas are products based on the composition  $\text{SiO}_2\cdot\text{K}_2\text{O}\cdot\text{MgO}\cdot\text{Al}_2\text{O}_3\cdot\text{ZrO}_2$ , with the addition of some fluorides to impart fluorescence in the prostheses, in a way similar to that encountered in the natural dentition. For this composition, the creaming process results in the nucleation and growth of tetrasilicate mica crystals within the glass. As with the lithium disilicate glass ceramic, the crystals are needle-like in shape and arrest the propagation of cracks through this material. Mechanical property measurements suggest the flexural strength is in the region of 120-150 MPa, which, when combined with the adhesion to tooth tissues, may just be adequate for posterior crowns but is insufficient for the construction of all-ceramic bridges.

The passage of light through the material is affected by the crystal size and difference in the refractive indices of the glass phase and the crystalline phase. If the crystals are smaller than the wavelength of visible light ( $0.4\text{-}0.7 \mu\text{m}$ ) the glass will appear transparent. The refractive index of the small mica crystals is closely matched to that of the surrounding glass phase, such that the tendency for light to scatter is lower than for the aluminous porcelains [5, 14].

## 2.2.3 Metal-Ceramic restorations

### 2.2.3.1 Porcelain condensation

Porcelain for porcelain jacket crowns (PJC<sub>s</sub>) and metal-ceramic restorations, as well as for other applications, is supplied as a fine powder that is designed to be mixed with water or another vehicle and condensed into the desired form. The powder particles are of a particular size distribution to produce the most densely packed porcelain when they are properly condensed. If the particles were of the same size, the density of packing would not be nearly as high as needed. Proper and thorough condensation is also crucial in obtaining dense packing of powder particles. Dense packing of the powder particles provides two benefits:

- 1) Lower firing shrinkage
- 2) Less porosity in the fired porcelain

This packing, or condensation, may be achieved by various methods, including the vibration, spatulation and brush techniques.

The first method uses mild vibration to pack the wet powder densely on the underlying framework. The excess water is blotted away with a clean tissue, and condensation occurs toward the blotted area. In the second method, small spatula is used to apply and smooth the wet porcelain. The smoothing action brings the excess water to the surface, where it is removed. The third method employs the addition of dry porcelain powder to the surface to absorb the water. The dry powder is placed by a brush to the side opposite from an increment of wet porcelain. As the water is drawn toward the dry powder, the wet particles are pulled together. Whichever be the method used, it is important to remember that the surface tension of the water is the driving force in condensation and that the porcelain must never be allowed to dry out until condensation is complete.

### 2.2.3.2 Firing procedure

The thermomechanical reactions between the porcelain powder components are virtually completed during the original manufacturing process. Therefore, the purpose of firing is simply to sinter the particles of powder together properly to form the restoration. Some chemical reactions do occur during prolonged firing times or multiple firings. Of particular importance are the observed changes in the leucite content of the

expansion (or high contraction crystal phase) whose volume fraction in the glass matrix can greatly affect the thermal contraction coefficient of the porcelain. Changes in the leucite content can cause the development of a thermal contraction coefficient mismatch between the porcelain and the metal and thus can produce stresses during cooling that are sufficient to cause crack formation in the porcelain.

The condensed porcelain mass is placed in front of or below the muffle of a preheated furnace (approximately 650°C for low fusing porcelain). This preheating procedure permits the remaining water vapour to dissipate. Placement directly of the condensed mass into even a moderately warm furnace results in a rapid production of steam, thereby introducing voids or fracturing large sections of the veneer. After preheating for 5 minutes, the porcelain is placed into the furnace, and the firing cycle is initiated.

The size of powder particles influences not only the degree of condensation of the porcelain but also the soundness or apparent density of the final product. At the initial firing temperature, the voids are occupied by the atmosphere of the furnace. As the sintering of the particles begins, the porcelain particles bond at their points of contact. As the temperature is raised, the sintering glass gradually flows to fill up the air spaces. However, air becomes trapped in the form of voids because the fused mass is too viscous to allow all the air to escape. An aid in the reduction of porosity in dental porcelain is “vacuum firing”.

Vacuum firing reduces the porosity in the following way. When the porcelain is placed into the furnace, the powder particles are packed together with air channels around them. As the air pressure inside the furnace muffle is reduced to about one tenth of the atmospheric pressure by the vacuum pump, the air around the particles is also reduced to this pressure. As the temperature rises, the particles sinter together and closed voids are formed within the porcelain mass. The air inside these closed voids is isolated from the furnace atmosphere. At a temperature about 55°C below the upper firing temperature, the vacuum is released and the pressure inside the furnace increases by a factor of ten. The voids are compressed to one tenth of their original size, and the total volume of porosity is accordingly reduced [1, 15].

### 2.2.3.3 Add-on glazing and shading materials

Porcelains for PFM, PJC, porcelain veneers, or even denture teeth may be characterized with stains and glazes to provide a more lifelike appearance. The fusing temperature of glazes is reduced by the addition of glass modifiers that lower the chemical durability of glazes somewhat. Stains are simply tinted glazes and are therefore subjected to the same chemical durability problems. However, most of the currently available glazes have adequate durability if they are as thick as 50  $\mu\text{m}$  or more.

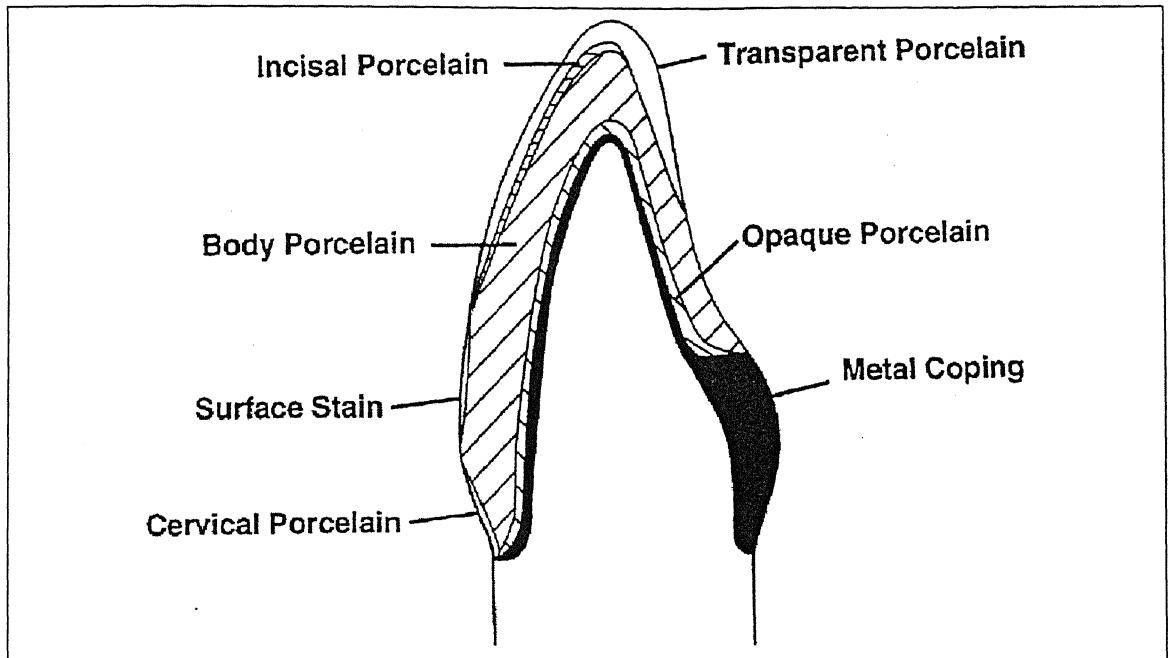
One method of ensuring that the applied characterizing stains will be permanent is to use them internally. Internal staining and characterization can produce a lifelike result, particularly when simulated enamel craze lines and other features are built into the porcelain rather than merely applied to the surface. The disadvantage of internal staining and characterization is that the porcelain must be stripped completely if the colour or characterization is unsuitable [1, 16].

### 2.2.3.4 Cooling

The proper cooling of a porcelain restoration from its firing temperature to room temperature is the subject of considerable controversy. The catastrophic fracture of glass that has been subjected to sudden changes in the temperature is a sufficiently familiar experience that most clinicians are cautious about exposing dental porcelain to rapid cooling after firing. The cooling of dental porcelain, however, is a complex matter, particularly when the porcelain is fused to a metallic substrate. Multiple firing of the metal-ceramic restoration can cause the coefficient of thermal contraction of the porcelain to increase and can actually make it more likely to crack or craze because of tensile stress development.

The chief limitation to the use of an all-porcelain crown in fixed prosthodontics is its lack of tensile and shear strength. A method of minimizing this disadvantage is to fuse the porcelain directly to a metal coping that fits the prepared tooth. Such a metal-ceramic restoration in Fig. 2.10.

The metal on the facial side is approximately 0.3-0.5 mm thick. It is veneered with opaque porcelain approximately 0.3 mm in thickness. The body porcelain is about 1mm thick [1].



**Fig. 2.10:** Porcelain used in the construction of a metal-ceramic crown.

### 2.2.3.5 Technical aspects of metal-ceramic restorations

This type of restoration is generally fabricated by a dental technician. The casting procedures are similar to those used for the casting of inlays and crowns. Because of the high melting temperature of the alloys, gypsum-bonded investments cannot be used and a phosphate-bonded investment must be used [1].

The casting should be carefully cleaned to ensure a good bond to the porcelain. In addition to cleaning, there are several other factors, which influence the bond strength between metal and ceramic. The factors that contribute to strong bond are:

- a) **Chemical bond:** Nonprecious element in an alloy produces metal oxides at the surface of the alloy, which produces a chemical bond with the porcelain. To create a uniform bond an oxide layer, which is uniform both in thickness and composition, is needed. Alloy with too much surface oxide after oxidation can lead to lowered bond strength. Therefore, it is important to blast the alloy with  $\text{Al}_2\text{O}_3$  following oxidation. An oxide layer is developed after every firing.

In case of carbon contamination, to which Pd base alloys and alloys with high Pd contents are susceptible, the carbon can react with oxygen to form carbon monoxide and/ or carbon dioxide forming bubbles in the ceramic. These bubbles at the interface between alloy and opaque may also decrease the bond strength. Increased carbon contents can be caused by an incorrect torch adjustments or the usage of graphite crucibles.

- b) **Mechanical bond:** Mechanical bond is very important for a clinical performance of metal-ceramic restorations. Removing casting oxides as well as properly sandblasting the alloy with 100-150  $\mu\text{m}$  aluminium oxide helps create a mechanical bond. Sandblasting with aluminium oxide helps create a keying affect, which provides a good surface for retention of the porcelain.
- c) **Coefficient of thermal expansion:** CTE needs be correct to achieve a proper bond. We may have created sufficient bonding strengths by using a fine grain alloy to produce a homogeneous oxide layer and used 100-150  $\mu\text{m}$  aluminium oxide to create a strong mechanical bond, but if the CTE of the alloy does not correspond to the CTE of the porcelain we will not create a proper bond. As porcelains cannot withstand tensile stresses, they have to be soft under compression. This is achieved only if the alloy contracts more than the

porcelain during cooling. Therefore, it is very important that the CTE of the alloy must be slightly higher than the CTE of the porcelain [17, 18].

#### 2.2.3.6 Benefits and drawbacks of metal-ceramic restorations

The properly made crown is stronger and more durable than the ordinary PJC. However, a long span bridge of this type may be subject to bending strains, and the porcelain may crack or fracture because of its low ductility. These difficulties can be partly overcome with proper restoration design. Proper occlusal relationships are also particularly important for this type of restoration.

The most outstanding advantages of metal-ceramic restorations are the permanent aesthetic quality of the properly designed reinforced ceramic unit and their resistance to fracture. Unlike similar acrylic resin veneered structures there is almost no wear of the porcelain by abrasion or change in colour because of microleakage between the veneer and the metal. Furthermore, as shown in one clinical study, the fracture rate of metal-ceramic crowns as well as bridges is as low as 2.3% after 7.5 years.

A slight advantage of PFM restorations over all-ceramic restoration is that less tooth structure needs to be removed to provide the proper bulk for the crown, especially if metal only is used on occlusal and lingual surfaces. High rigidity of the structure is needed to prevent fracture of the porcelain. Although the modulus of elasticity of the porcelain is moderately high, its low tensile and shear strengths indicate a low maximal flexibility because, in brittle fracture, the breaking strength and proportional limit coincide. As a result, only limited elastic deformation of the porcelain can be tolerated. It follows, therefore, that even with a high modulus of elasticity; considerable bulk of the crown cannot be conspicuously out of line with the anatomic form of the adjacent teeth. Therefore, bulk of the natural tooth may need to be sacrificed to provide adequate space to ensure adequate fracture resistance and aesthetics.

In spite of several disadvantages, the metal-ceramic restorations are the most widely used system in fixed prosthodontics today

In addition to classification of dental porcelain based on the nature of supporting structure, it can also be classified according to their firing temperatures. A typical classification is as follows:

High fusing	1300°C
Medium fusing	1101-1300°C

Low fusing	850-1100°C
Ultra low fusing porcelain	<850°C

The medium-fusing and high-fusing types are used for the production of denture teeth. The low-fusing and ultra-low-fusing porcelains are used for crown and bridge construction. Some of the ultra-low-fusing porcelains are used for titanium and titanium alloys because of their low contraction coefficients that closely match those of the metals and because the low firing temperatures reduce the risk for growth of the metal oxide. However, some of these ultra-low-fusing porcelains contain enough leucite to raise their thermal contraction coefficients as high as those of conventional low-fusing porcelains [1].

### 2.3 Properties of dental porcelain

The characteristic properties of porcelain are hardness, strength, aesthetic, opacity, translucency, insolubility in oral environment, biocompatibility and resistance to thermal and chemical attack. The thermal conductivity and the coefficient of thermal expansion are similar to those of enamel and dentine, so, in the presence of a good marginal seal, marginal percolation is less likely to be a problem.

The particle size distribution of dental porcelain is critical in ensuring that the particles pack together as tightly as possible, in order that the shrinkage on firing is minimized. The average particle size is generally in the region of 25  $\mu\text{m}$ , with a wide range distribution of other particles sizes such that the smaller particles fill the spaces in between the larger particles. Some porcelain powders have a multimodal particle distribution to increase the packing density.

Although the compressive strength of dental porcelain is high (350-550 MPa), its tensile strength is very low (20-60 MPa), which is typical of a brittle solid. The material being primarily a glass lacks any fracture toughness. The maximum strain that a glass can withstand is less than 0.1%. Glasses are extremely sensitive to the presence of surface microcracks, and this represents one of the major drawbacks in the use of dental porcelain. On cooling from the furnace temperature, the outside of the porcelain will cool more rapidly than the interior, particularly as the porcelain has a low thermal conductivity. The outside surface contracts more than the inside initially, resulting in a compressive load on the outside and the residual tensile on the inside, as the interior is being prevented from shrinking by the outside skin. Another major drawback is the potential to cause abrasive

wear on the opposing dentition. Other properties that needed to be considered are castibility, moldability, injectability, machinability and abrasion resistance strength. They are critical characteristics because the new all-ceramic restorations use them in their fabrication.

The application of a glaze with a slightly lower coefficient of expansion would potentially fill in the cracks and also place the surface under compression. Unfortunately, this is not possible on the fitting surface of the crown, as it may result in the crown not strong enough to be used for the manufacture of multiunit bridges, and problems even arose for anterior porcelain jacket crowns, especially when they were used in situations of heavy occlusion. The tiny surface flaws in the interior of the crown act as initiating sites for catastrophic failure. The inherently low tensile strength of feldspathic porcelains (<60 MPa) restricted their use to the very low stress bearing anterior applications. The answer is to provide a high strength support for the porcelain and nowadays a number of different systems are available such as metal-ceramic restorations, reinforced ceramic core systems or resin-bonded ceramics.

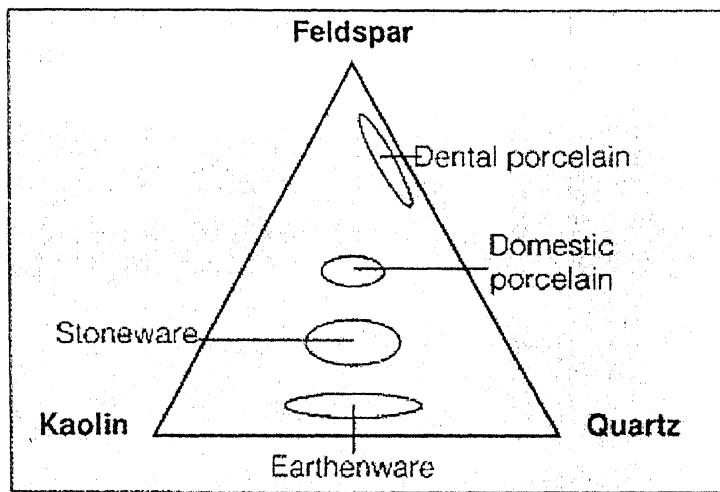
Leucite is particularly an important component in dental porcelain because it affects the optical properties, thermal expansion, strength and hardness of porcelain. Leucite is potassium-aluminium-silicate mineral with a large coefficient of thermal expansion ( $20-25 \times 10^{-6}/^{\circ}\text{C}$ ) compared with feldspar glasses (they have coefficient of thermal expansion somewhat less than  $10 \times 10^{-6}/^{\circ}\text{C}$ ). When potassium feldspar is mixed with various oxides and heated at temperatures ranging  $1150^{\circ}\text{C}$  to  $1530^{\circ}\text{C}$ , it undergoes incongruent melting to form crystals of leucite in a liquid glass. Incongruent melting is a process by which one material melts to form a liquid plus a different crystalline material. This tendency of feldspar to form leucite during incongruent melting is used to advantage in the manufacturing of porcelains for metal bonding. Also the softening of the glass phase during porcelain firing allows the porcelain powder particles to coalesce together. For dental porcelains, the process by which the particles coalesce together is called 'liquid phase sintering', a process controlled by diffusion between particles at a temperature sufficiently high to form a dense solid. The driving force for sintering is the decrease in energy caused by a reduction in surface area [16, 19]

One of the drawbacks of leucite containing porcelain is that it causes more abrasion to wear to opposing tooth structure because of high hardness of leucite. However, this can be decreased by using low fusing porcelain (LFC), which does not contain crystal

phase and has only glass phase. Low fusing porcelain has decreased hardness, which leads to decreased wear and abrasion on the opposing dentition [1, 5].

## 2.4 Composition of dental porcelain

The composition of dental porcelains has been given in various literatures with slight percentage variations of ingredients. One of the literature suggests that the earliest dental porcelain were mixtures of kaolin, feldspar and quartz and were quite different for earthen ware, stoneware and domestic porcelain, as indicated in Fig 2.11.



**Fig. 2.11:** Relative composition of ceramic products based on feldspar, kaolin and quartz.

It was not until 1838 that Elias [5] produced dental porcelain with the translucency and shades that reasonably matched those of natural teeth. The compositions for domestic & dental porcelain are given in Table 2.2.

**Table 2.2:** Composition of household and dental porcelain

Porcelain	% Kaolin	% Quartz	% Feldspar
Household	50	20-25	25-30
Dental	10	25	65

A large amount of literature can be found which deals with the composition and method of formulation of dental porcelains. One such literature suggests the ingredients of dental porcelain as follows:

**Table 2.3:** Composition of dental porcelain

Ingredients	Percentage (%)
Feldspar	81
Quartz	15
Kaolin	4
Metallic pigments	<1%

Kaolin is a hydrated aluminium silicate ( $\text{Al}_2\text{O}_2\text{SiO}_2\cdot2\text{H}_2\text{O}$ ) and acts as a binder, increasing the ability to mould the unfired porcelain. It is opaque, however, and when present, even in small quantities, causes lack of adequate translucency. Thus for all dental porcelains kaolin was omitted and the material could therefore be considered to be a feldspathic glass with crystalline inclusions of silica.

Quartz remains unchanged during the firing process and acts as a strengthening agent. It is present as a fine crystalline dispersion throughout the glassy phase that is produced by the melting of the feldspar. The feldspar fuses and when it melts, forms a glass matrix.

The feldspars are mixtures of potassium aluminosilicate ( $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ ) and sodium aluminosilicate, also known as albite ( $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ ). Feldspars are naturally occurring substances, so the ratio between the potash ( $\text{K}_2\text{O}$ ) and the soda ( $\text{Na}_2\text{O}$ ) will vary somewhat. This affects the properties of the feldspar, in that the soda tends to lower the fusion temperature and potash increases the viscosity of the molten glass.

During the firing of porcelain there is always the danger of excessive pyroplastic flow, which may result in rounding of the edges and loss of tooth form. It is important that correct amount of potash is present to prevent this. These alkalis are present either as a part of the feldspars, or they may be added as carbonates to ensure the correct ratio. The typical oxide composition of dental porcelain is presented in Table 2.4 [5].

**Table 2.4:** Typical oxide composition of a dental porcelain

Components	Weight percent
Silica ( $\text{SiO}_2$ )	63
Alumina ( $\text{Al}_2\text{O}_3$ )	17
Boric oxide ( $\text{B}_2\text{O}_3$ )	7
Potash ( $\text{K}_2\text{O}$ )	7
Soda ( $\text{Na}_2\text{O}$ )	4
Other oxides	2

A number of other ingredients will be present in dental porcelain powders. These include metal oxides, which provide the wide variety of colours of the porcelain; for example copper as a green pigment, titanium as a yellowish brown pigment and cobalt imparts a blue colour. A binder consisting of starch and sugar may also be present to help in the manipulation of the powders [8, 9].

In addition to compositions mentioned above, a large number of compositions can also be found in US PATENTS. These patents have given composition of dental porcelains used for metal-ceramic restorations, resin bonded ceramics and all ceramic restorations. The composition of dental porcelain varies with respect to their use. For example in metal-ceramic restorations, metal provides adequate strength, hardness, toughness and other desirable properties. Hence, the main function of porcelain here is to provide aesthetic properties. But in case of all ceramic restorations, core is also made up of ceramic; so its function becomes similar to that of metal in metal-ceramic restorations, that is, it should be strong enough to support the coating provided on it. Hence composition of this type of ceramic is different in comparison to the composition used for porcelain in metal-ceramic restorations. In the present study stress has been given on the composition of porcelains used for metal-ceramic restorations.

Most of the US PATENTS, which deal with porcelains used in metal-ceramic restorations, have not given separate compositions for different layers of porcelain coated on metal substructure. They have given overall composition of such porcelains. For example, US PATENT 5552350 has given composition of low fusing temperature porcelain which is as given in Table 2.5 [20].

**Table 2.5:** Composition of low fusing temperature dental porcelain

Ingredients	Weight percentage
SiO <sub>2</sub>	57-61
Al <sub>2</sub> O <sub>3</sub>	6.5-11.5
Na <sub>2</sub> O	10-11
K <sub>2</sub> O	8-16
Li <sub>2</sub> O	1-3
CaO	1.5-4
BaO	1.5-2.5
CeO <sub>2</sub>	0.5-2
Tb <sub>2</sub> O <sub>3</sub>	0.5-2

US PATENT 5591030 explained that purpose of applying dental porcelain in several layers on metal core is to improve bonding and aesthetic properties. It suggests first bonder powder is applied whose composition is as given in Table 2.6.

**Table 2.6:** composition of bonder layer

Compound	Weight percent (%)
SiO <sub>2</sub>	57.13
Na <sub>2</sub> O	6.63
CaO	1.47
K <sub>2</sub> O	11.47
Al <sub>2</sub> O <sub>3</sub>	15.7
B <sub>2</sub> O <sub>3</sub>	3.06
TiO <sub>2</sub>	3.7

This layer improves the bonding between opaque layer and metal core. Before applying on the metal core, bonder powder is mixed with modeling liquid so that paste can be made. After that layer preopaque layer is applied which increases the aesthetic property. The composition of preopaque layer is given in Table 2.7.

**Table 2.7:** Composition of preopaque layer

Compound	Weight percent (%)
SiO <sub>2</sub>	51.8
Na <sub>2</sub> O	5.96
CaO	1.27
K <sub>2</sub> O	10.02
Al <sub>2</sub> O <sub>3</sub>	14.4
B <sub>2</sub> O <sub>3</sub>	2.796
TiO <sub>2</sub>	3.09
SnO <sub>2</sub>	10.63

The preopaque layer is followed by another layer namely opaque layer whose composition is as given in Table 2.8.

**Table 2.8:** Composition of opaque layer

Compound	Weight percent (%)
SiO <sub>2</sub>	54.8
Na <sub>2</sub> O	7
CaO	14
K <sub>2</sub> O	10.6
Al <sub>2</sub> O <sub>3</sub>	15
B <sub>2</sub> O <sub>3</sub>	2.3
TiO <sub>2</sub>	8.8

Thereon dentin and enamel powders of following compositions are applied which is given in Table 2.9.

**Table 2.9:** Composition of dentine and enamel layers

Compound	Weight percent (%)
SiO <sub>2</sub>	57.5
Na <sub>2</sub> O	6.7
CaO	1.8
K <sub>2</sub> O	11.2
Al <sub>2</sub> O <sub>3</sub>	17.1
B <sub>2</sub> O <sub>3</sub>	5.7

All powders are mixed with modeling liquid before application. All layers are fired at around 800°C. After applying dentine and enamel layers this may be followed by a glaze firing using common painting colours such as Vitachrom "L" and Vitachrom Delta stains painting colours. The firing likewise is conducted at about 800°C [7].

According to US PATENT 4879136, the composition of opaque powder, which is mixed with organic liquid such as glycerol, glycol or dimethylsulphoxide to form a paste and applied as first layer on the metal core, is given in Table 2.10.

All oxides are ingredients of a ground glass frit. Only TiO<sub>2</sub> is admixed to ensure the presence of the fine powder, which is added to insure good spreadability. The paste formed has organic liquid and opaque powder in the ratio of 1:3 [21-23]. Small amount of Alum or other stabilizing salts are also included in the paste. The size distribution for opaque powder not including TiO<sub>2</sub> is given in Table 2.11. On an average TiO<sub>2</sub> has a grain size less than about 1µm [6].

**Table 2.10:** Composition of opaque layer

Compound	Weight percent (%)
SiO <sub>2</sub>	42
Al <sub>2</sub> O <sub>3</sub>	12
K <sub>2</sub> O	8
Na <sub>2</sub> O	4
LiO <sub>2</sub>	0.5
CaO	1.5
B <sub>2</sub> O <sub>3</sub>	1
ZrO <sub>2</sub>	1
SnO <sub>2</sub>	10
TiO <sub>2</sub>	20

**Table 2.11:** Size distribution of opaque powder

Percentage of particles	Weight percent (%)
21	<5 $\mu\text{m}$
66	<12 $\mu\text{m}$
98	<24 $\mu\text{m}$
100	<40 $\mu\text{m}$

This patent explains that after applying the opaque paste on metallic framework, the system is dusted with a layer of coarse ceramic powder having an average grain size of between 40 $\mu\text{m}$  to 100 $\mu\text{m}$ . The ceramic powder used for dusting must have a thermal stability such that at least a substantial portion of grain structure is maintained under conditions of firing so that sand paper consistency of the surface is obtained. The composition of this coarse ceramic powder is as given in Table 2.12.

**Table 2.12:** Composition of coarse ceramic powder

Compound	Weight percent (%)
SiO <sub>2</sub>	56
Al <sub>2</sub> O <sub>3</sub>	13
K <sub>2</sub> O	9
Na <sub>2</sub> O	4
CeO <sub>2</sub>	18

For dentine and enamel layers, the use of additional opacifying oxides such as TiO<sub>2</sub> or SnO<sub>2</sub> is not needed because of their high opacifying effect. In place of these opacifying oxides some pigments are used. To prevent the separation of dentine and enamel powder from the modeling liquid (glycerol) in the paste, it is preferred that about 3% of hydrophobic aerosil be added to the modeling liquid. The spreadability of dentine and enamel paste is not as good as compared to that of opaque layer because of the absence of the fine (less than 2 $\mu$ m) particles, but high spreadability of these layers is not needed because applications of these layer is made easy due to the presence of coarse grains onto the opaque layer of paste [6].

Some patents also deal with two phase dental porcelain in which leucite is the crystalline phase dispersed in feldspathic glass matrix. US PATENT 5653791 gives the composition of such porcelain, which is given in Table 2.13 [24].

**Table 2.13:** Composition of two-phase dental porcelain

Compound	Percent weight (%)	Percent weight (%)	Percent weight (%)	Percent weight (%)
SiO <sub>2</sub>	57-66	58-65	62.1	58
Al <sub>2</sub> O <sub>3</sub>	7-15	8-14	9.8	58
K <sub>2</sub> O	7-15	11-15	14.2	15
Na <sub>2</sub> O	7-12	7.5-11	7.6	8.1
Li <sub>2</sub> O	0.5-3	0.7-1.5	1.1	1.5
CaO	0-3	0-1.5	1.0	1.0
MgO	0-7	0-5	1.9	1.0
F	0-4	0-3	1.9	1.0
CeO <sub>2</sub>	0-1	0-0.5	0.4	0.4
CTE (°C)	$12-17.5 \times 10^{-6}$	$12-17.5 \times 10^{-6}$	$15 \times 10^{-6}$	$17.4 \times 10^{-6}$
Maturing Temperature (°C)	790-1050	880-1000	815	850

## 2.5 Dental Alloys

### 2.5.1 Historical perspective

The history of dental casting alloys has been influenced by three major factors: (1) the technological changes of dental prostheses; (2) metallurgical advancements; and (3) price changes of the noble metals since 1968.

Taggart's [1] presentation to the New York Odontological Group in 1907 on the fabrication of cast inlay restorations often has been acknowledged as the first reported application of the *lost wax technique* in dentistry. The inlay technique described by Taggart was an instant success. It soon led to the casting of complex inlays such as onlays, crowns, fixed partial dentures, and removable partial denture frameworks. Because pure gold did not have the physical properties required of these dental restorations, existing jewelry alloys were quickly adopted. These gold alloys were further strengthened with copper, silver, or platinum.

In 1932, the dental materials group at The National Bureau of Standards surveyed the alloys being used and roughly classified them as Type I (soft: Vicker hardness number [VHN] between 50 and 90), Type II (medium: VHN between 90 and 120), Type III (Hard: VHN between 120 and 150), and Type IV (extra hard: VHN  $\geq 150$ ). At that time, some tarnish tests indicated that alloys with a gold content lower than 65% to 75% tarnished too readily for dental use.

In the following years, several patents were issued for alloys containing palladium as a substitute for platinum. By 1948, the composition of dental noble metal alloys for cast metal restorations had become rather diverse. With these formulations, the tarnishing tendency of the original alloys apparently had disappeared. It is now known that in gold alloys, palladium is added to counteract the tarnish potential of silver.

In the late 1950s, a breakthrough occurred in dental technology that was to influence significantly the fabrication of dental restorations. This was the successful veneering of a metal substructure with dental porcelain. Until that time, dental porcelain had a markedly lower coefficient of thermal expansion than did gold alloys, making it impossible to attain a bond between the two structural components. It was found that adding both platinum and palladium to gold would lower the alloy's coefficient of thermal contraction sufficiently to ensure physical compatibility between the porcelain veneer and the metal substructure. By serendipity, the melting range of the alloy was also raised sufficiently to permit firing of the porcelain onto the gold-based alloy at 1040°C (1900°F) without deforming the metal substructure.

The base metal removable partial denture alloys were introduced in the 1930s. Since that time, both nickel-chromium and cobalt-chromium formulations have become increasingly popular compared with conventional Type IV gold alloys, which previously were the predominant metals used for such prostheses. The obvious advantages of the base metal alloys are their lighter weight, increased mechanical properties (although exceptions to this statement may be found), and reduced costs. For these reasons, such nickel and cobalt based alloys have largely replaced the noble metal alloys for removable partial dentures.

The success of the base metal alloys for constructing a removable partial denture framework led to some early interest in applying these same alloys to fabricate other types of restorations. However, intensive research into the characteristics of alloys for that purpose did not start until the 1970s, which was stimulated by the rapidly

escalating price of noble metals. Naturally, the track record of the nickel-chromium and cobalt-chromium partial denture alloys made them a logical choice for evaluation as probable alternatives for other dental applications. Likewise, by 1978 the price of gold was climbing so rapidly that attention was focused on the noble metal alloys to reduce the precious metal content, yet retaining the advantages of the noble metals for dental use.

### 2.5.2 Desirable properties of dental casting alloys

Cast metals are used in dental laboratories to produce inlays, onlays, crowns, conventional all-metal bridges, metal-ceramic bridges, resin-bonded bridges, endodontic posts, and removable partial denture frameworks. The metal must exhibit biocompatibility, ease of melting, casting, brazing (or soldering) and polishing, little solidification shrinkage, minimal reactivity with the mold material, good wear resistance, high strength and sag resistance (metal-ceramic alloys), and excellent tarnish and corrosion resistance.

### 2.5.3 Classification of dental casting alloys

#### 2.5.3.1 Alloys for all-metal and resin veneer restorations

**High noble and noble metal alloys:** In 1927, the Bureau of standards ( now the National Institute of Standards and Technology) established gold casting alloy Type I through IV according to dental function, with hardness increasing from Type I to Type IV. Typical compositions of these alloys are given in Table 2.14. Properties of eight alloys used for all-metal ( and resin veneer) restorations and four alloys used for metal-ceramic restorations are given in Table 2.15.

Based on the 1989 revision of Specification No. 5 by the American Dental Association (ADA) , the following four alloy types are classified by their properties and not by their compositions:

Type I (soft)- small inlays, easily burnished and subject to very slight stress

Type II (medium)- inlays subject to moderate stress, including thick three-quarter crowns , abutments, pontics, and full crowns

Type III (hard)- inlays subject to high stress, including thin three-quarter crowns, thin cast backings, abutments, pontics, full crowns, and denture bases, and short-span fixed partial dentures.

Type IV (extra hard)- inlays subject to very high stresses, including denture base

crowns are often made of this type). The compositions of these alloys are usually based on a majority of either gold or silver; gold alloys can be age hardened by an appropriate heat treatment.

**Table 2.14:** Composition Range (weight percent) of Traditional Types I to IV Alloys and Four Metal-Ceramic Alloy

Alloy Type	Main Elements	Au	Cu	Ag	Pd	Sn, In, Fe, Zn, Ga
I	High noble (Au base)	83	6	10	0.5	Balance
II	High noble (Au base)	77	7	14	1	Balance
III	High noble (Au base)	75	9	11	3.5	Balance
III	Noble (Au base)	46	8	39	6	Balance
III	Noble (Ag base)			70	25	Balance
IV	High noble (Au base)	56	14	25	4	Balance
IV	Noble (Ag base)	15	14	45	25	Balance
Metal-ceramic	High noble (Au base)	52			38	Balance
Metal-ceramic	Noble (Pd base)			30	60	Balance
Metal-ceramic	High noble (Au base)	88		1	7(+4 Pt)	Balance
Metal-ceramic	Noble (Pd base)	0-6	0-15	0-6	88	Balance

**Table 2.15:** Physical properties of some modern noble metal dental alloys

Alloy Type	Main Elements	Melting Range (°C)	Density (g/cm <sup>3</sup> )	Yield Strength (MPa)	Hardness (VHN)	Percent Elongation
I	High noble	943-960	16.6	103	80	36
II	High noble	924-960	15.9	186	101	38
III	High noble	924-960	15.5	207 H275	121 H182	39 H19
	Noble	843-916	12.8	241 H586	138 H231	30 H13
	Ag-Pd noble	1021-1099	10.6	262 H323	143 H154	10 H8
IV	High noble	921-943	15.2	275	149	35 H7
	High noble	871-932	13.6	372 H720	186 H254	38 H2
	Noble	930-1021	11.3	434 H586	180 H270	10 H6
Metal-ceramic	*High noble	1271-1304	13.5	572	220	20
	Noble	1232-1304	10.7	462	189	20
	<sup>1</sup> High noble	1149-1177	18.3	450	182	5
	Noble	1155-1302	10.6-11.5	476-685	235-270	10-34

\* White coloured

<sup>1</sup>Yellow coloured

H, Age-hardened condition. Other values are for the quenched (softened) condition.

**Silver-Palladium alloys:** These alloys are white and have predominantly silver in composition along with substantial amounts of palladium (at least 25%) that provides nobility and promote the silver tarnish resistance. They may or may not contain copper and a small amount of gold. Casting temperatures are in the range of the yellow gold alloys. The copper-free Ag-Pd alloys may contain 70% to 72% silver and 25% palladium and may have physical properties of a Type III gold alloy. Other silver-based alloys might contain roughly 60% silver, 25% palladium, and as much as 15% or more of copper and may have properties more like a Type IV gold alloy. Despite early reports of poor castability, the Ag-Pd alloys can produce acceptable castings. The major limitation of Ag-Pd alloys, in general, and the Ag-Pd-Cu, in particular is their greater potential for tarnish and corrosion.

**Titanium and Titanium alloys:** These metals can be used for all-metal and metal-ceramic restorations as well as for removable partial denture frameworks.

**Aluminium Bronze alloy:** The aluminium bronze family of alloys consist of one alloy which has been approved by ADA for all-metal restorations. The alloy contains between 81 and 88 wt % copper, 7 to 11 wt % aluminium, 2 to 4 wt % nickel, and 1 to 4 wt % iron. Little clinical data are available on this aluminium bronze dental alloy. There is a potential for copper alloys to react with sulfur to form copper sulfide, which may tarnish the surface of this alloy in the same manner that silver sulfide darkens the surface of gold-base or silver-base alloys that contain a significant amount of silver.

### 2.5.3.2 Alloys for metal-ceramic restorations

The chief objection to the use of dental porcelain as a restorative material is its low tensile and shear strength. Although porcelain can resist compressive stresses with reasonable success, substructure design does not permit shapes in which compressive stress is the principal force.

A method by which this disadvantage can be minimized is to bond the porcelain directly to a cast alloy substructure made to fit the prepared tooth. If a strong bond is attained between the porcelain veneer and the metal, the porcelain veneer is reinforced. Thus, the risk of brittle fracture can be avoided or, at least, minimized.

**High noble alloys for metal-ceramic restorations:** The compositions of high noble alloys normally used for metal-ceramic restorations are given in Table 2.16.

**Table 2.16:** Typical composition for High noble alloys for metal-ceramic restorations

Alloy Class	Principal Elements* (wt %)				
	Au	Pt	Pd	Ag	Ga
Au-Pt-Pd or Au-Pd-Pt (0-4.99% Ag)	81	6	11		
	87	5	6	1	
	85	8	5		
Au-Pd-Ag (5-11.99% Ag)	77	3	10	9	
	75		13	9	
Au-Pd-Ag (≥12% Ag)	49		32	15	
	53		27	16	
	45		40	16	
Au-Pd (no Ag)	52		39		2
	52		37		
	51		39		
	51		39		

\* Bond forming elements such as tin and indium are not shown

**Noble alloys for metal-ceramic restorations:** The compositions of noble alloys for metal-ceramic restorations are given in Table 2.17.

**Table 2.17:** Composition of Noble alloys for metal-ceramic restorations

Alloy Class	Principal Elements* (wt %)						
	Au	Pt	Pd	Ag	Cu	Co	Ga
Pd-Au (no Ag)	35		57				5
	30		60				
Pd-Au-Ag	32	3	42	13			
	19		48	26			
	16		62	6			
Pd-Au-Ag-Ga	6		75	6.5			6
	6		75	6			6
Pd-Ag			60	28			
			54	38			
			58	30			
Pd-Cu-Ga	2		79		10		9
	2		80		9		9
			74		15		9
Pd-Co			78			10	
			79			8	1.5
			88			4	8

\* Bond forming elements such as tin and indium are not shown

**Base metal alloys for metal-ceramic restorations:** A survey of 1000 dental laboratory owners in 1978 revealed that only 29% of these laboratories were using Ni-Cr or Co-Cr alloys for metal-ceramic restorations. In 1980 and 1981, the percentage of laboratories using these base metal alloys increased to 66% and 70%, respectively, because of the unstable price of noble metal during this period. Most of these dental laboratories indicated a preference for Ni-Cr alloys over Co-Cr alloys. Although the increased acceptance of these alloys during this period was greatly influenced by the rapidly fluctuating international cost of gold and other noble metals, the subsequent decline in the cost of noble metals has had a small effect on reversing this trend. Ni-Cr-Be alloys have retained their popularity despite the potential toxicity of beryllium and the allergenic potential of nickel. In some regional areas, an increase in the use of palladium alloys has been observed.

Since the development of cobalt-chromium alloys for cast dental appliances in 1928 and the subsequent introduction of Ni-Cr and Ni-Co-Cr alloys in later years, base metal alloys have demonstrated widespread acceptance in the United States as the predominant choice for the fabrication of removable partial denture frameworks. Compared with ADA-certified Type IV gold alloys, the cobalt-based and nickel-based alloys, as well as pure titanium exhibit lower cost, lower density, greater stiffness, higher hardness, and comparable clinical resistance to tarnish and corrosion.

Most Ni-Cr alloys for crowns and fixed partial denture prostheses contain 61 to 81 wt % nickel, 11 to 27 wt % chromium, and 2 to 5 wt % molybdenum. Typical compositions of several commercial alloys used in the past (some of which are currently used) for metal ceramic restorations are given in Table 2.18. Chromium is essential to provide passivation and corrosion resistance. Other alloy formulations include Cr-Co and Fe-Cr. These alloys may also contain one or more of the following elements: aluminium, beryllium, boron, carbon, cobalt, copper, cerium, gallium, iron, manganese, niobium, silicon, tin, titanium, and zirconium. The Co-Cr alloys typically contain 53 to 67 wt % cobalt, 25 to 32 wt % chromium, and 2 to 6 wt % molybdenum. Recently, chemically pure titanium and Ti-Al-V alloys have been introduced for metal-ceramic restorations.

The **physical and mechanical properties** of some Ni-Cr based alloys and a gold alloy for metal-ceramic restorations is given in Table 2.19 which can be used for comparative study. The composition of such Ni-Cr alloys is given in Table 2.20 [1, 25].

**Table 2.18:** Typical base Metal Alloys for Metal-Ceramic Restorations

Alloy Name (supplier)	Composition (wt %)						
	Ni	Co	Cr	Be	Mo	W	Ru
Rexillium III (Jeneric/Pentron)	76	0.3	14	1.8	5		
Litecast B (Williams Dental Co.)	78		13	1.7	4		
Neptune (Jeneric/Pentron)	62		22		9		
Forte (Unitek/3M)	62		22		9		
Genesis II (J.F.Jelenko & Co.)		53	27				3
Ultra 100 (Unitek/3M)		52	28				
Novarex (Jeneric/Pentron)		55	25			10	5

**Table 2.19:** Physical and Mechanical Properties of Base Metal Alloys and a Gold Alloy.

Properties	A	B	C	D	E	F	Gold Alloy
Tensile strength (MPa)	1142	1139	1355	661	540	703	490
Yield Strength (MPa)	591	782	838	360	260	543	400
Modulus of elasticity (MPa) X 10 <sup>3</sup>	207	190	210	193	154	208	88
Percent elongation (%)	23.9	11.6	18	27.9	27.3	2.3	9.1
Vicker's hardness (DPH)	293	348	357	211	175	316	161
Density (g/cm <sup>3</sup> )	8.1	8	7.9	8	8.7	8.3	18.3
Porcelain bond (MPa)	97.9	51	87.6	70.3	80.7	106.2	111

**Table 2.20:** Composition of Base Metal Alloys for Metal Ceramic Restorations

Element	A	B	C	D	E	F
Nickel	80.75	79.67	78.51	68.96	80.86	68.75
Chromium	12.58	13.24	19.47	16.54	11.93	19.57
Iron	0.34	0.11	0.43	0.37	0.20	0.38
Aluminium	3.42	3.87	0.21	4.15	2.95	
Molybdenum	1.53	1.52		5.10	1.87	4.22
Silicon	0.29	0.30	1.10	0.83	0.18	2.72
Beryllium	0.57	0.65			1.55	
Copper	0.15				0.13	1.54
Manganese	0.13	0.12		3.05	0.14	1.24
Cobalt				0.42		
Tin						1.25

## 2.6 Clinical performance

On the basis of recent surveys, the use of base metal alloys has shown a rapid increase, largely at the expense of traditional high noble metal-ceramic alloys. Laboratories report a high degree of satisfaction with most of these alloys in terms of the casting, finishing, and the application of porcelain veneers.

Comparison of the long-term (10 to 15 years) clinical performance of these alloys has been difficult, because data based on well-controlled scientific clinical studies are not available. One 5-year study compared several nickel-based alloys with a gold alloy. In addition, a 10-year study that includes several other base metal (Ni-Cr) alloy systems is in progress, and the final 5-year preliminary results have been reported. Although 5-year data provide important information, the time period is relatively short for detecting clinically significant differences as to long-term behavior. However, both studies indicate that during a period of 5 years the performance of the base metal alloys was acceptable and was comparable to that of a gold-containing alloy.

The performance of any restoration is related to multiple factors, for example, the design of the appliance, the skill and accuracy with which it has been fabricated, and the properties of the materials used. The successful use of the base metal

alloys requires some modification of the laboratory procedures, but it appears to provide clinically acceptable and durable restorations. In the 10-year study it has been noted that all restorations are deteriorating slightly; however, at 5 years, only 4% of all restorations failed and had to be removed. This included those fabricated using the control alloy. Of these failures, slightly less than half could be associated with the materials themselves, and the rest were the result of patient-related reasons or technical errors in the making of the restorations [1].

## **Chapter 3**

# **Experimental Procedures**

### **3.1 Raw materials**

#### **3.1.1 Dental ceramics**

The dental ceramics that were used for characterization in the present work were wash opaque (WO 3000), dentine (EN1, A3 3053) and enamel (EN2 3072). These powders were supplied by Vita Zahnfabrik Company, Germany.

#### **3.1.2 Dental alloy**

The dental alloy used for characterization in the present work was Bellabond N (BBN 81006). This was supplied by International Dental Systems, India.

#### **3.1.3 Ceramic powders**

The ceramic powders used for the purpose of synthesization were Silicon Oxide ( $\text{SiO}_2$ ), Alumina ( $\text{Al}_2\text{O}_3$ ), Calcium Carbonate ( $\text{CaCO}_3$ ), Sodium Carbonate ( $\text{Na}_2\text{CO}_3$ ), Titanium Oxide ( $\text{TiO}_2$ ), Barium Carbonate ( $\text{BaCO}_3$ ), Borax ( $\text{Na}_2\text{B}_4\text{O}_7.10\text{H}_2\text{O}$ ), Zirconia ( $\text{ZrO}_2$ ), Magnesium Carbonate ( $\text{MgCO}_3$ ), Cerium Oxide ( $\text{CeO}_2$ ), Lithium Carbonate ( $\text{Li}_2\text{O}_3$ ), Ferric Oxide ( $\text{Fe}_2\text{O}_3$ ), Potassium carbonate ( $\text{K}_2\text{CO}_3$ ) and Stannous Oxide ( $\text{SnO}_2$ ) of LR grade. The name of the suppliers and the relevant specifications are given in Table 3.1.

**Table 3.1:** Supplier Company and specifications of different ceramic powders

Powder Name	Grade	Supplier Company	Specifications
Silicon oxide	LR	E. Merck (India), Ltd.	Minimum assay: 98%
Barium carbonate	LR	E. Merck (India), Ltd.	Minimum assay: 99-101%
Cerium oxide	LR	E. Merck (India), Ltd.	Minimum assay: 99%
Zirconia	LR	E. Merck (India), Ltd.	Minimum assay: 99.5%
Titanium oxide	LR	E. Merck (India), Ltd.	Minimum assay: 99%
Potassium carbonate	LR	E. Merck (India), Ltd.	Minimum assay: 98%
Aluminium oxide	LR	E. Merck (India), Ltd.	Minimum assay: 99%
Magnesium carbonate	LR	E. Merck (India), Ltd.	Minimum assay: 99%
Calcium carbonate	LR	E. Merck (India), Ltd.	Minimum assay: 98.5%
Lithium carbonate	LR	Titan Biotech (India), Ltd.	Minimum assay: 99%
Stannous oxide	LR	Titan Biotech (India), Ltd.	Minimum assay: 98.5%
Sodium carbonate	LR	Titan Biotech (India), Ltd.	Minimum assay: 99.5%
Ferric oxide	LR	CDH (P) Ltd., India	Minimum assay: 85%
Borax	LR	Loba Chemie Pvt. Ltd., India	Minimum assay: 99-103%

### 3.2 Powder characterization

The as received dental ceramic powders were characterized for their size distribution, quantitative elemental analysis and crystalline behaviour. The laboratory synthesized dental ceramic powders were also characterized for their size distribution and crystalline behaviour. In addition to that these synthesized powders were also characterized for their glass transition temperature and crystallization temperature.

#### 3.2.1 Particle size and size distribution

Particle size determination was carried out using a laser-scattering size analyzer (model: Economy, Laser Klasse 1; supplier: Fritsch, Germany). Low angle Fraunhofer light scattering by monochromatic laser and dispersed particles were used in this case. Particles were suspended in a moving fluid. The suspension was made using 1 to 3 grams of powder in approximately 60 ml of distilled water with 10 % sodium metaphosphate. The particles were passed through a laser beam in a circulating water stream. The light is scattered after the interaction with the particles, and the intensity is measured by strategically placed detectors. Particle size affects both the intensity and angular extent of scattering. With coherent light the angle of scattering varies inversely with the particle diameter. The scattering depends on the refractive index of the particle in the suspending medium, the wavelength of light, and the particle size and shape.

#### 3.2.2 SEM/EDS analysis

The quantitative elemental analysis of the three as received dental ceramic powders were carried out in a Kevex Sigma Energy Dispersive Spectroscopy (EDS) detector connected with JEOL, JSM-840A, Scanning Electron Microscope, in the secondary electron (SE) mode.

The quantitative elemental analysis of sample by EDS works on the principle that a focused beam of electrons is rastered across a sample surface and synchronized with the raster of a cathode ray tube. The secondary electrons or backscattered electrons produced are detected and used to modulate the brightness of the CRT. The stored signal is then a detailed map of the sample surface. Since the electron beam also generates the emission of x-rays

characteristic of the elements present, energy dispersive analysis of the x-rays provides a means of elemental identification.

Ceramics are known as bad conductors of electricity hence it is imperative to make them conducting first. The three powders were placed on three different cylindrical blocks. Some methyl alcohol was added to the powders so that they would behave as properly adhered masses during the study. The thickness of powder masses was kept very small over blocks to avoid charging of particles during experiment. After that the powders were given a coating of Au-Pd for 1 hr to make them conducting. The sample conditions during analysis were as follows:

kV → 15.0

Beam current → 1.3 Pico Amps

Working Distance → 12.0 mm

Tilt Angle → 0.0 Degrees

Takeoff Angle → 35 Degrees

Solid Angle\* Beam Current → 0.0

### **3.2.3 TG/DTA analysis**

The laboratory synthesized wash opaque 1 and 2 powders were characterized for their glass-transition and crystallization temperatures in a Pyris Diamond Thermogravimetric/Differential Thermal Analysis (TG/DTA) instrument (supplier: Perker Elmer Inc., USA).

The Diamond TG/DTA works on the principle that when a weight change occurs on the sample side, the beam is displaced. This movement is detected optically and the drive coil current is changed to return the displacement to zero. The detected drive coil current change is proportional to the sample weight changes and this is the output as the TG signal. The DTA detects the temperature difference between the sample holder and the reference holder using the electromotive force of thermocouples, which are attached to the holders. This differential is the output as DTA signal.

One to two grams of the sample was placed in an alumina crucible and the reference material (alumina) was placed in a platinum crucible. The samples were brought upto 100°C without maintaining any heating rate. After that wash opaque 1 powder was

heated from 100°C to 1000°C at a heating rate of 15°C/min and from 1000°C to 1200°C at a heating rate of 20°C/min. Wash opaque 2 powder was heated from 100°C to 1200°C at a heating rate of 15°C/min. The flow rate of nitrogen was maintained at 200 ml/min during heating for both the samples. After that the samples were cooled at a rate of 15°C/min upto room temperature.

The TG/DTA instrument is connected to a computer for the purpose of saving and recording all experimental data [26].

### 3.2.4 X-ray Diffraction analysis

X-ray diffraction studies on the powders were carried out to determine whether a material is crystalline or amorphous. Indexing of X-ray diffraction patterns were carried out by matching peak coordinate value with the standard values from Joint Commission for Powder Diffraction Standard (JCPDS) cards (ed. 1996).

X-ray diffraction studies on the powders were carried out on Rich Seifert & Co., Germany, ISO Debyeflex- 2002 diffractometer. Powders were kept in a square holder having very small thickness. Some methyl alcohol was added on the powders so that they would be properly adhered during diffraction study. The various parameters used during the experiment are given below,

Target (Radiation) → Cu (K $\alpha$ )

Wavelength,  $\lambda$  → 1.542 X 10 $^{-10}$  m

Scanning Speed → 3°C/min, (in 2 $\theta$ )

Counts/min → 50, 000

Time constant → 10s

Amperage → 20 mA

Voltage → 30 kV

The X-ray machine is connected with computer. While scanning the sample, computer saved all the data (intensity and angle). From these data the intensity vs. angle graphs were plotted.

### 3.2.5 Chemical analysis

The as received three dental ceramic powders were sent for compositional analysis at NML, Jamshedpur. The analyses were carried out using standard methods.

### 3.3 Powder preparation for laboratory synthesis of wash opaque, dentine and enamel

**Composition:** The composition of laboratory synthesized wash opaque 1 was taken from US PATENT 4879136 whereas compositions of laboratory synthesized dentine 1 and enamel 1 were taken from US PATENT 5591030 with some little changes. The compositions taken for laboratory synthesized wash opaque 2, dentine 2 and enamel 2 were based on compositional analyses results of the as received powders. Tables 3.2 to 3.7 show the compositions taken for laboratory synthesized wash opaque (1&2), dentine (1&2) and enamel (1&2).

**Table 3.2:** Composition chosen for synthesis of wash opaque 1

Components	Wt%
SiO <sub>2</sub>	42
Al <sub>2</sub> O <sub>3</sub>	12
K <sub>2</sub> O	8.0
Na <sub>2</sub> O	4.0
B <sub>2</sub> O <sub>3</sub>	1.0
Li <sub>2</sub> O	0.5
CaO	1.5
TiO <sub>2</sub>	20
SnO <sub>2</sub>	10
ZrO <sub>2</sub>	1.0

**Table 3.3:** Composition chosen for synthesis of wash opaque 2

Components	Wt%
SiO <sub>2</sub>	48.65
Al <sub>2</sub> O <sub>3</sub>	20.00
K <sub>2</sub> O	8.77
Na <sub>2</sub> O	4.50
B <sub>2</sub> O <sub>3</sub>	2.00
MgO	1.00
Li <sub>2</sub> O	1.00
CaO	1.50
TiO <sub>2</sub>	1.00
SnO <sub>2</sub>	6.58
ZrO <sub>2</sub>	5.00

**Table 3.4:** Composition chosen for laboratory synthesis of dentine 1

Components	Wt%
SiO <sub>2</sub>	57.5
Al <sub>2</sub> O <sub>3</sub>	17.1
K <sub>2</sub> O	11.2
Na <sub>2</sub> O	6.7
B <sub>2</sub> O <sub>3</sub>	2.0
CaO	1.8
CeO <sub>2</sub>	3.7

**Table 3.5:** Composition chosen for laboratory synthesis of dentine 2

Components	Wt%
SiO <sub>2</sub>	59.97
Al <sub>2</sub> O <sub>3</sub>	13.86
K <sub>2</sub> O	10.64
Na <sub>2</sub> O	6.20
B <sub>2</sub> O <sub>3</sub>	2.00
MgO	0.406
TiO <sub>2</sub>	0.064
ZrO <sub>2</sub>	0.108
CaO	2.42
CeO <sub>2</sub>	3.70
Fe <sub>2</sub> O <sub>3</sub>	0.62

**Table 3.6:** Composition chosen for laboratory synthesis of enamel 1

Components	Wt%
SiO <sub>2</sub>	57.5
Al <sub>2</sub> O <sub>3</sub>	17.1
K <sub>2</sub> O	11.2
Na <sub>2</sub> O	6.7
B <sub>2</sub> O <sub>3</sub>	2
ZrO <sub>2</sub>	3.7
CaO	1.8

**Table 3.7:** Composition chosen for laboratory synthesis of enamel 2

Components	Wt%
SiO <sub>2</sub>	63.38
Al <sub>2</sub> O <sub>3</sub>	13.00
K <sub>2</sub> O	11.34
Na <sub>2</sub> O	6.44
B <sub>2</sub> O <sub>3</sub>	1.00
BaO	0.49
CaO	1.73
ZrO <sub>2</sub>	2.53
TiO <sub>2</sub>	0.079

**Mixing:** Two compositions each for wash opaque, dentine and enamel were made by taking various oxides, carbonates (for potassium oxide, sodium oxide, magnesium oxide, barium oxide, calcium oxide and lithium oxide their corresponding carbonates were used) and borax (for B<sub>2</sub>O<sub>3</sub>) in correspondence to their weight percent as mentioned in Tables 2 to 7. An electronic balance (supplier: Mettler, AE200, USA) having 0.0001 accuracy was used for weighing the different constituents. The balance was calibrated using a series of standard weights. After weighing, six different compositions (two each for wash opaque, dentine and enamel) were prepared by mixing their respective ingredients in a Granite (stone) Mortar and Pestle for one hour to ensure complete homogenization of the powder mixture.

### 3.4 Melting

Melting of the powder mixtures was carried out in a superkanthal-heated program controlled furnace (Model No: HT 04/17, max<sup>m</sup> temp. 1750°C) supplied by Nabertherm GmbH, Germany. After mixing, the compositions were transferred to six different cylindrical alumina crucibles (supplier: Kumar manufacturing Co., India) and put inside the furnace. The maximum temperature that these crucibles can withstand is 1800°C. The samples were heated from room temperature to 1500°C at a heating rate of 4°C/min. The

atmosphere used was air for all the samples. The samples were isothermally held at that temperature for 22-24 hrs so that complete fusion of ceramic powders could take place. After that the samples were taken out from furnace at that temperature and water quenched to avoid crystallization of samples. After that the samples were taken out from the crucibles by breaking them. The samples so obtained were in the solid form. For heat treatment purpose the samples were kept in as such whereas for X-ray diffraction and TG/DTA analysis parts of the samples were grounded in powder form in the size range suitable for these analyses. The grinding was done in a Granite (stone) Mortar and Pestle.

### **3.5 Heat treatment**

The solids of wash opaque 1 & 2 were given heat treatment in a wire bound horizontal tubular furnace (Lab made, Max<sup>m</sup> temp. 1100°C).

For **wash opaque 1** following temperatures were chosen for heat treatment:

- 1) Room Temperature (RT) to 500°C; holding at 500°C for 1 hr; again heating from 500°C to 750°C; holding at 750°C for 1 hr.
- 2) Room Temperature (RT) to 500°C; holding at 500°C for 1 hr; again heating from 500°C to 850°C; holding at 850°C for 1 hr.
- 3) Room Temperature (RT) to 500°C; holding at 500°C for 1 hr; again heating from 500°C to 950°C; holding at 950°C for 1 hr.
- 4) Room Temperature (RT) to 500°C; holding at 500°C for 1 hr; again heating from 500°C to 1050°C; holding at 1050°C for 1 hr.
- 5) Room Temperature (RT) to 600°C; holding at 600°C for 1 hr; again heating from 600°C to 750°C; holding at 750°C for 1 hr.
- 6) Room Temperature (RT) to 600°C; holding at 600°C for 1 hr; again heating from 600°C to 850 °C; holding at 850°C for 1 hr.
- 7) Room Temperature (RT) to 600°C; holding at 600°C for 1 hr; again heating from 600°C to 950°C; holding at 950°C for 1 hr.
- 8) Room Temperature (RT) to 600°C; holding at 600°C for 1 hr; again heating from 600°C to 1050°C; holding at 1050°C for 1 hr.
- 9) Room Temperature (RT) to 700°C; holding at 700°C for 1 hr; again heating from 700°C to 850°C; holding at 850°C for 1 hr.

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10) Room Temperature (RT) to 700°C; holding at 700°C for 1 hr; again heating from 700°C to 950°C; holding at 950°C for 1 hr.

11) Room Temperature (RT) to 700°C; holding at 700°C for 1 hr; again heating from 700°C to 1050°C; holding at 1050°C for 1 hr.

For **wash opaque 2** following heat treatment temperatures were chosen:

1) Room Temperature (RT) to 500°C; holding at 500°C for 1 hr; again heating from 500°C to 750°C; holding at 750°C for 1 hr.

2) Room Temperature (RT) to 500°C; holding at 500°C for 1 hr; again heating from 500°C to 850°C; holding at 850°C for 1 hr.

3) Room Temperature (RT) to 500°C; holding at 500°C for 1 hr; again heating from 700°C to 950°C; holding at 950°C for 1 hr.

4) Room Temperature (RT) to 600°C; holding at 600°C for 1 hr; again heating from 600°C to 750°C; holding at 750°C for 1 hr.

5) Room Temperature (RT) to 600°C; holding at 600°C for 1 hr; again heating from 600°C to 850°C; holding at 850°C for 1 hr.

6) Room Temperature (RT) to 600°C; holding at 600°C for 1 hr; again heating from 600°C to 950°C; holding at 950°C for 1 hr.

7) Room Temperature (RT) to 700°C; holding at 700°C for 1 hr; again heating from 700°C to 850°C; holding at 850°C for 1 hr.

8) Room Temperature (RT) to 700°C; holding at 700°C for 1 hr; again heating from 700°C to 950°C; holding at 950°C for 1 hr.

In all heat treatments the atmosphere kept was air and the heating rate employed was 3°C/ min. All the samples after reaching their final temperature were taken out of furnace and were air-cooled. For microstructural analysis the heat-treated samples were kept in solid form whereas for X-ray diffraction and particle size analysis the samples were grounded into powder form in a Granite (Stone) Mortar and Pestle.

For laboratory synthesized dentine (1&2) and enamel (1&2) no heat treatments were done [27]

### **3.6 Microstructural studies**

**Optical microscopy:** The heat-treated samples as well as the samples obtained just after melting (glass) were cold mounted since their height was not sufficient for holding. The samples were polished on 1.0 to 4.0 grades of emery papers followed by fine wheel polishing with suspended 0.03  $\mu\text{m}$  size alumina in distilled water. The etchant used was 10% HF solution. Etching was carried out for 1-2 minutes by swabbing method. The microstructures of these samples were observed before and after etching using Leitz Labor Lux 12MES Image Analyzer.

### **3.7 Dental alloy characterization**

The as received dental alloy was characterized for quantitative elemental analysis by EDS. The other tests done on dental alloy were bulk hardness measurement and X-ray diffraction analysis. For EDS analysis the alloy was not given a coating of Au-Pd, as its conductivity was good. The alloy was only polished on 1.0 to 4.0 grades of emery paper followed by cleaning in running water. For XRD the alloy was used in solid form having smooth surface.

**Rockwell Hardness:** The bulk hardness of alloy was determined in Indentec Rockwell Hardness Tester Machine (supplier: Indentec Hardness Testing Machines Ltd, UK). The load applied was 150 Kgf and indentation time of 60 seconds was maintained. The reading was noted from the Rockwell hardness tester machine.

## Chapter 4

# Experimental Results

### 4.1 Results of compositional analysis

The three as received dental ceramic powders and a dental alloy were first examined for their composition to know what type of ingredients they consist of. The three powders were sent for chemical analysis at NML, Jamshedpur. The results were cross-checked by taking elemental composition of these powders by EDS. For dental alloy only EDS analysis was done to know the elemental composition. The compositional analysis result for as received wash opaque, dentine and enamel obtained from NML, Jamshedpur is given in Tables 4.1, 4.3 and 4.5 respectively. The EDS results for as received wash opaque, dentine, enamel and a dental alloy are given in Tables 4.2, 4.4, 4.6 and 4.7 respectively.

#### 4.1.1 Wash opaque

**Table 4.1:** Compositional analysis result of wash opaque from NML, Jamshedpur

Compound	Wt %	
	Actual	Out of 100
SiO <sub>2</sub>	41.100	48.65
Al <sub>2</sub> O <sub>3</sub>	20.300	24.02
K <sub>2</sub> O	7.410	8.77
Na <sub>2</sub> O	3.800	4.50
CaO	1.260	1.50
TiO <sub>2</sub>	0.845	1.00
SnO <sub>2</sub>	5.560	6.58
ZrO <sub>2</sub>	4.225	5.00

**Table 4.2:** Elemental analysis result of wash opaque by EDS

Element	Wt %			
	Trial 1	Trial 2	Trial 3	Average
Si	15.59	18.05	18.10	17.25
Al	0.80	2.85	1.85	1.84
K	11.60	11.35	11.40	11.45
Na	0.35	1.65	0.00	0.67
Ti	12.88	6.55	11.55	10.33
Sn	28.55	22.56	25.45	25.52
Zr	29.04	35.5	30.19	31.58
Ca	1.19	1.49	1.46	1.38

## 4.1.2 Dentine

Table 4.3: Compositional analysis result of dentine from NML, Jamshedpur

Compound	Wt %	
	Actual	Out of 100
SiO <sub>2</sub>	48.400	59.970
Al <sub>2</sub> O <sub>3</sub>	12.800	15.860
K <sub>2</sub> O	8.590	10.640
Na <sub>2</sub> O	5.010	6.200
MgO	0.328	0.406
TiO <sub>2</sub>	0.052	0.064
ZrO <sub>2</sub>	0.087	0.108
CaO	1.950	2.420
CeO <sub>2</sub>	2.980	3.700
Fe <sub>2</sub> O <sub>3</sub>	0.5	0.620

Table 4.4: Elemental analysis of dentine by EDS

Element	Wt %			
	Trial 1	Trial 2	Trial 3	Average
Si	28.89	22.85	27.54	26.42
Al	1.34	1.86	1.82	1.67
K	18.27	12.67	17.52	16.15
Na	0.17	0.35	0.35	0.29
Ti	3.37	3.45	3.58	3.47
Zr	37.88	45.48	38.36	40.57
Ce	4.46	4.54	4.89	4.63
Mg	0.00	0.60	0.52	0.37
Ca	3.17	5.89	3.89	4.32
Fe	2.44	2.31	1.53	2.09

#### 4.1.3 Enamel

**Table 4.5:** Compositional analysis result of enamel from NML, Jamshedpur

Compound	Wt %	
	Actual	Out of 100
SiO <sub>2</sub>	47.700	63.380
Al <sub>2</sub> O <sub>3</sub>	12.400	16.380
K <sub>2</sub> O	8.540	11.340
Na <sub>2</sub> O	4.850	6.440
BaO	0.368	0.490
TiO <sub>2</sub>	0.059	0.079
ZrO <sub>2</sub>	0.047	0.063
CaO	1.300	1.730

**Table 4.6:** Elemental composition of enamel by EDS

Element	Wt %			
	Trial 1	Trial 2	Trial 3	Average
Si	25.64	28.92	28.62	27.72
Al	2.13	1.75	2.07	1.98
K	14.48	13.37	13.85	13.90
Na	0.28	0.35	0.32	0.32
Ti	1.04	0.79	0.87	0.90
Zr	49.87	47.74	47.56	48.39
Ba	4.39	5.67	4.85	4.97
Ca	2.17	1.41	1.86	1.81

#### 4.1.4 Dental Alloy

**Table 4.7:** Elemental composition of dental alloy by EDS

Element	Wt %			
	Trial 1	Trial 2	Trial 3	Average
Ni	59.96	59.92	59.96	59.94
Cr	24.67	24.63	24.64	24.64
Si	0.92	0.92	0.93	0.92
Mn	7.81	7.85	7.82	7.83
Fe	1.40	1.41	1.39	1.40
Nb	0.37	0.39	0.39	0.38
Mo	4.86	4.88	4.86	4.86

#### 4.2 XRD results

The as received powders were analyzed for determining their crystalline behavior in an X-ray diffractometer. Phase identification was done by comparing the three strong intensity values of XRD plots with standard JCPDS cards. The XRD plots for as received wash opaque and dentine are given in Fig. 4.1. XRD plots for as received enamel and dental alloy are given in Fig. 4.2. XRD analysis of dental alloy was done to cross-check the results of EDS. The XRD plots for laboratory synthesized wash opaque 1 having nucleation temperature 500°C (holding time 1 hr) and crystallization temperatures 750°C and 850°C (holding time in each case 1 hr) are given in Fig. 4.3. The XRD plots for laboratory synthesized wash opaque 1 having nucleation temperature 500°C (holding time 1 hr) and crystallization temperatures 950°C and 1050°C (holding time in each case 1 hr) are given in Fig. 4.4. Similarly, XRD plots for laboratory synthesized wash opaque 1 having nucleation temperature 600°C (holding time 1 hr) and crystallization temperatures 750°C and 850°C (holding time in each case 1 hr) are given in Fig. 4.5. XRD plots for laboratory synthesized wash opaque 1 having nucleation temperature 600°C (holding time 1 hr) and crystallization temperatures 950°C and 1050°C (holding time in each case 1 hr) are given in Fig. 4.6. XRD

plots for laboratory synthesized wash opaque 1 having nucleation temperature 700°C (holding time 1 hr) and crystallization temperatures 850°C and 950°C (holding time in each case 1 hr) are given in Fig. 4.7. Similarly, XRD plot for laboratory synthesized wash opaque 1 having nucleation temperature 700°C (holding time 1 hr) and crystallization temperature 1050°C (holding time 1 hr) is given in Fig. 4.8. XRD plots for laboratory synthesized wash opaque 2 having nucleation temperature 500°C (holding time 1 hr) and crystallization temperatures 750°C and 850°C (holding time in each case 1 hr) are given in Fig. 4.9. Fig. 4.10 have XRD plot of laboratory synthesized wash opaque 2 at nucleation temperature 500°C (holding time 1 hr) and crystallization temperature 950°C (holding time 1 hr). XRD plots for laboratory synthesized wash opaque 2 having nucleation temperature 600°C (holding time 1 hr) and crystallization temperatures 750°C and 850°C (holding time in each case 1 hr) are given in Fig. 4.11. XRD plot for laboratory synthesized wash opaque 2 having nucleation temperature 600°C (holding temperature 1 hr) and crystallization temperature 950°C (holding temperature 1 hr) is given in Fig. 4.12. XRD plots for laboratory synthesized wash opaque 2 having nucleation temperature 700°C (holding temperature 1 hr) and crystallization temperatures 850°C and 950°C (holding temperature in each case 1 hr) are given in Fig. 4.13. XRD plots of laboratory synthesized dentine 1 & 2 and enamel 1 & 2 are given in Fig. 4.14 and 4.15 respectively.

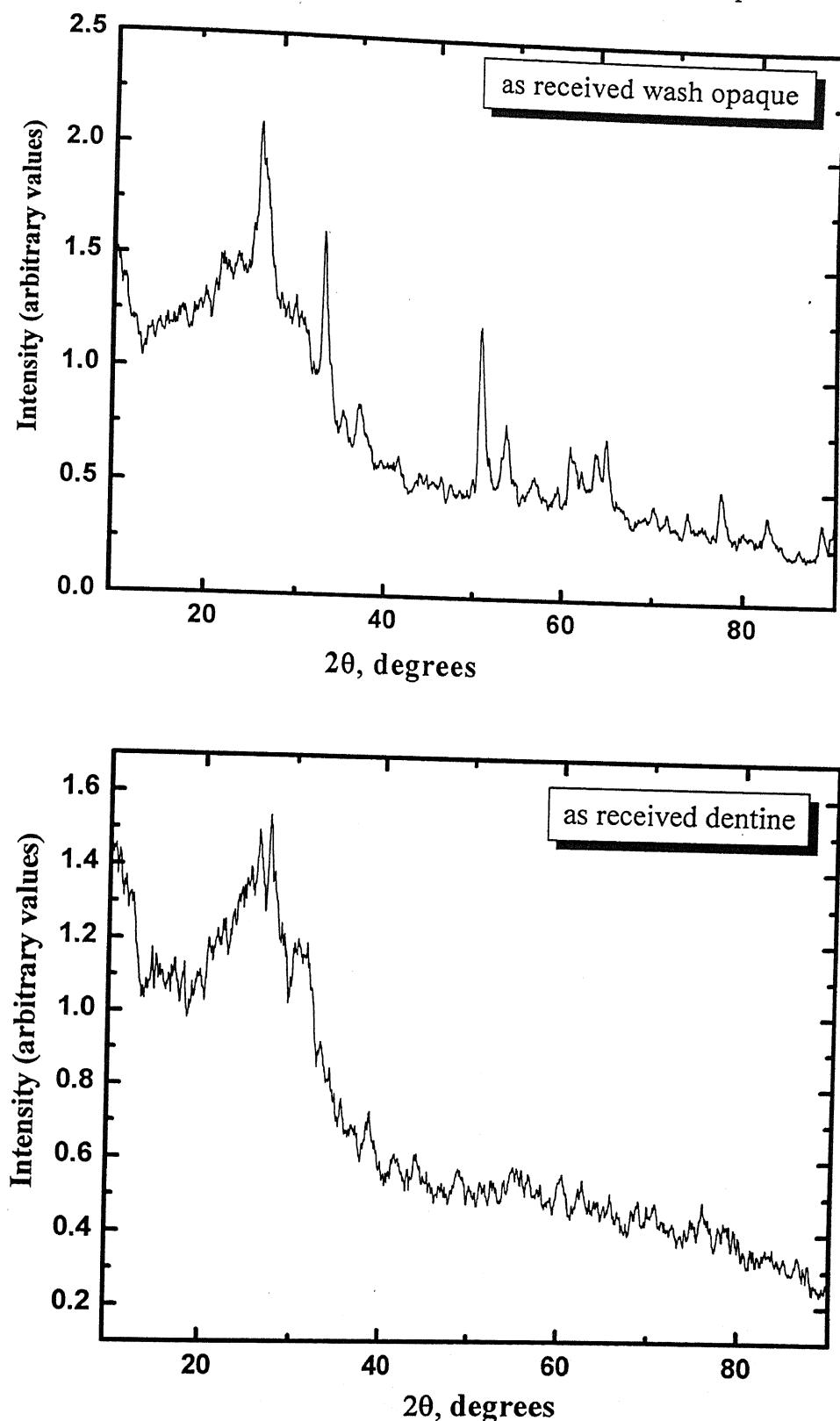


Fig. 4.1: XRD plots of as received wash opaque and dentine.

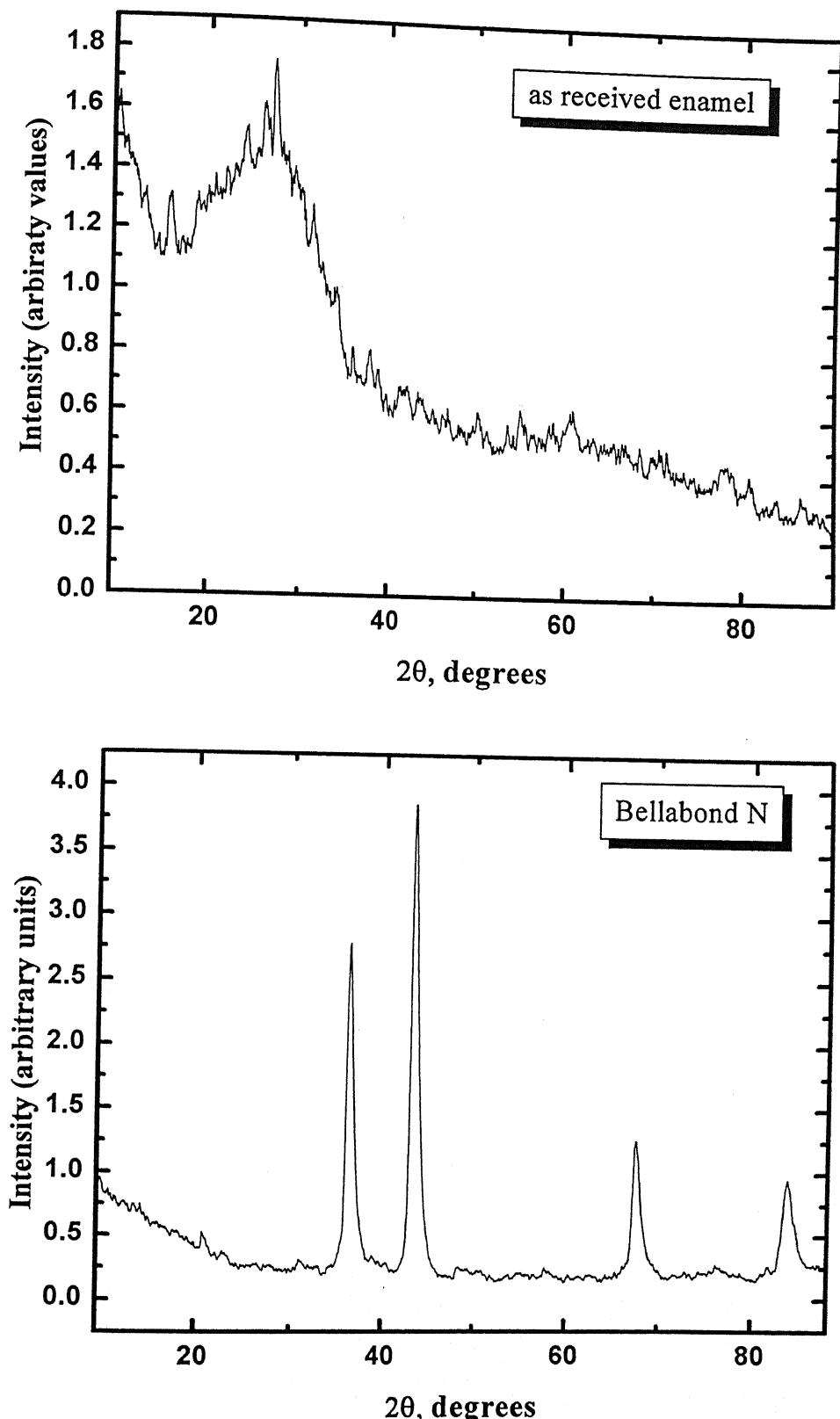
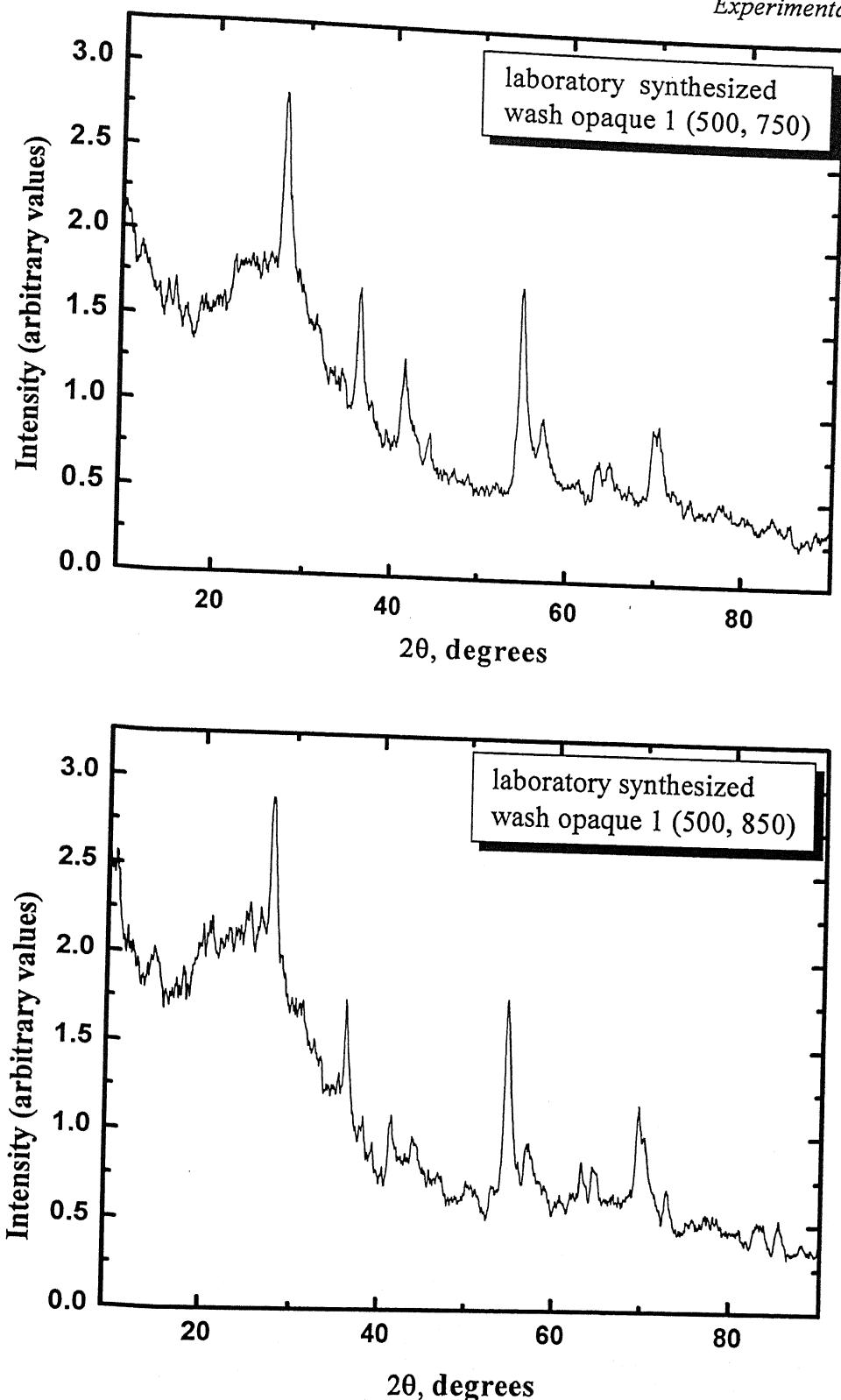


Fig. 4.2: XRD plots of as received enamel and dental alloy.



**Fig. 4.3:** XRD plots of laboratory synthesized wash opaque 1 at nucleation temperature 500°C (holding time 1hr) and crystallization at 750°C and 850°C, (holding time in each case 1 hr).

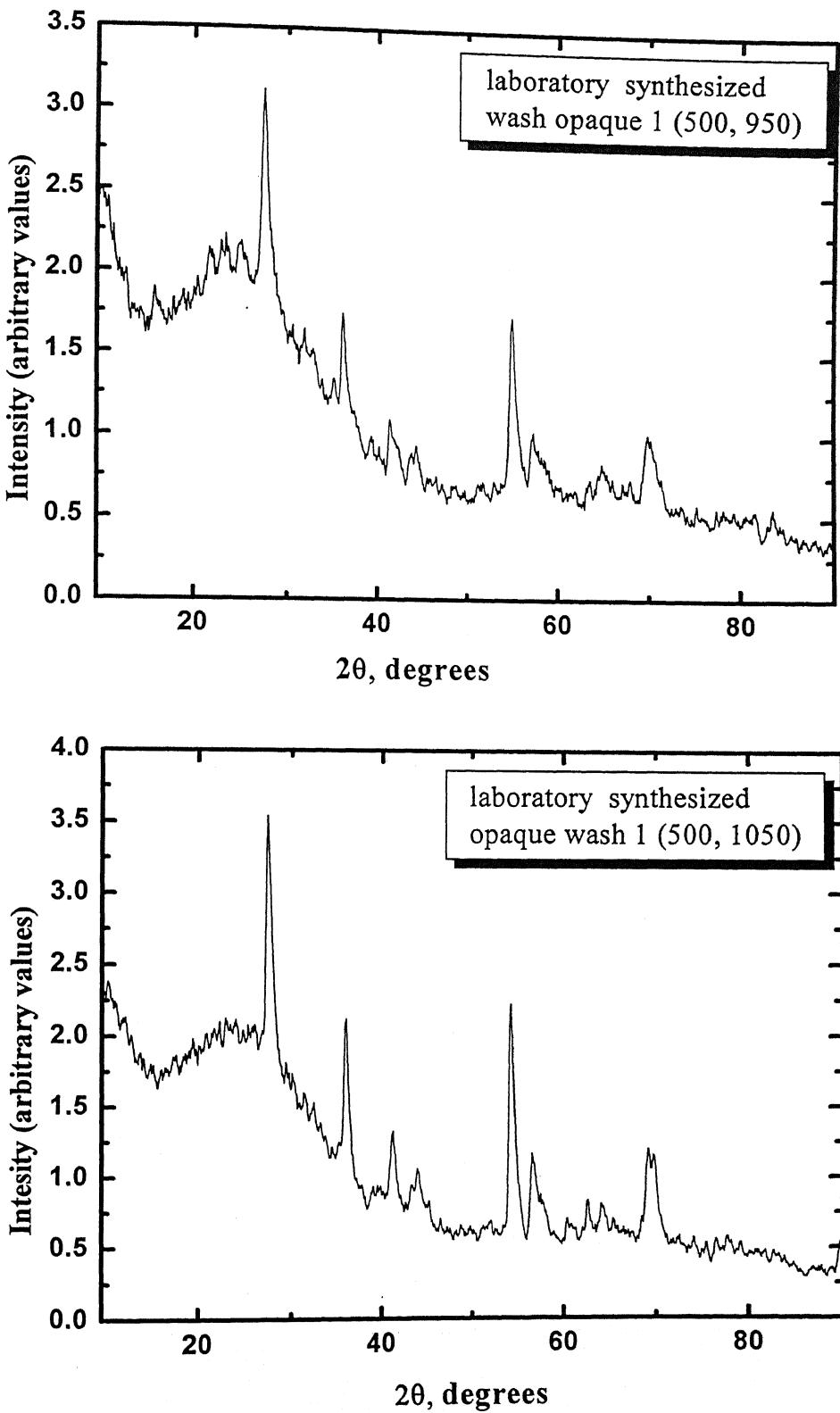


Fig. 4.4: XRD plots of laboratory synthesized wash opaque 1 at nucleation temperature  $500^{\circ}\text{C}$  (holding time 1hr) and crystallization at  $950^{\circ}\text{C}$  and  $1050^{\circ}\text{C}$  (holding time in each case 1 hr).

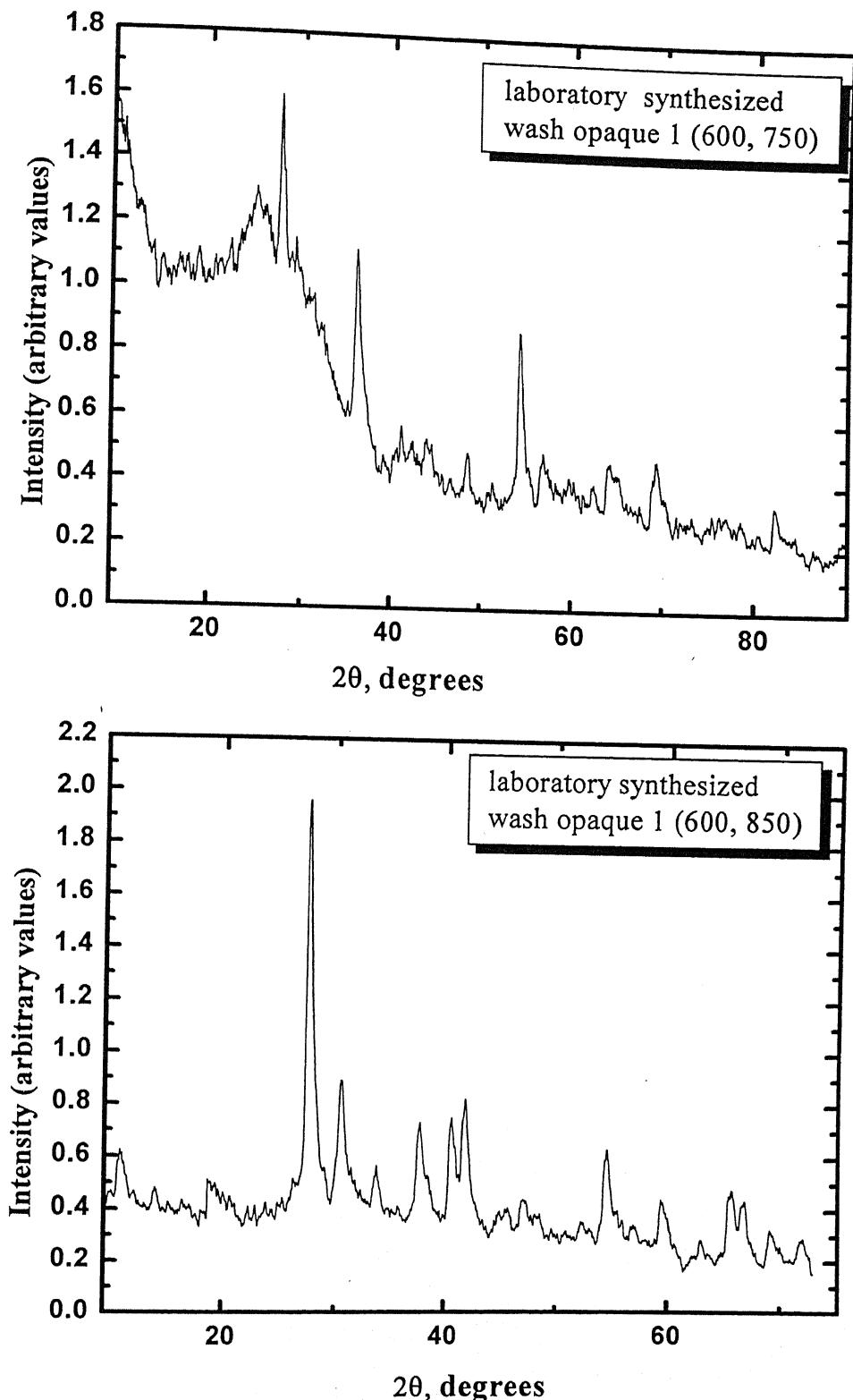
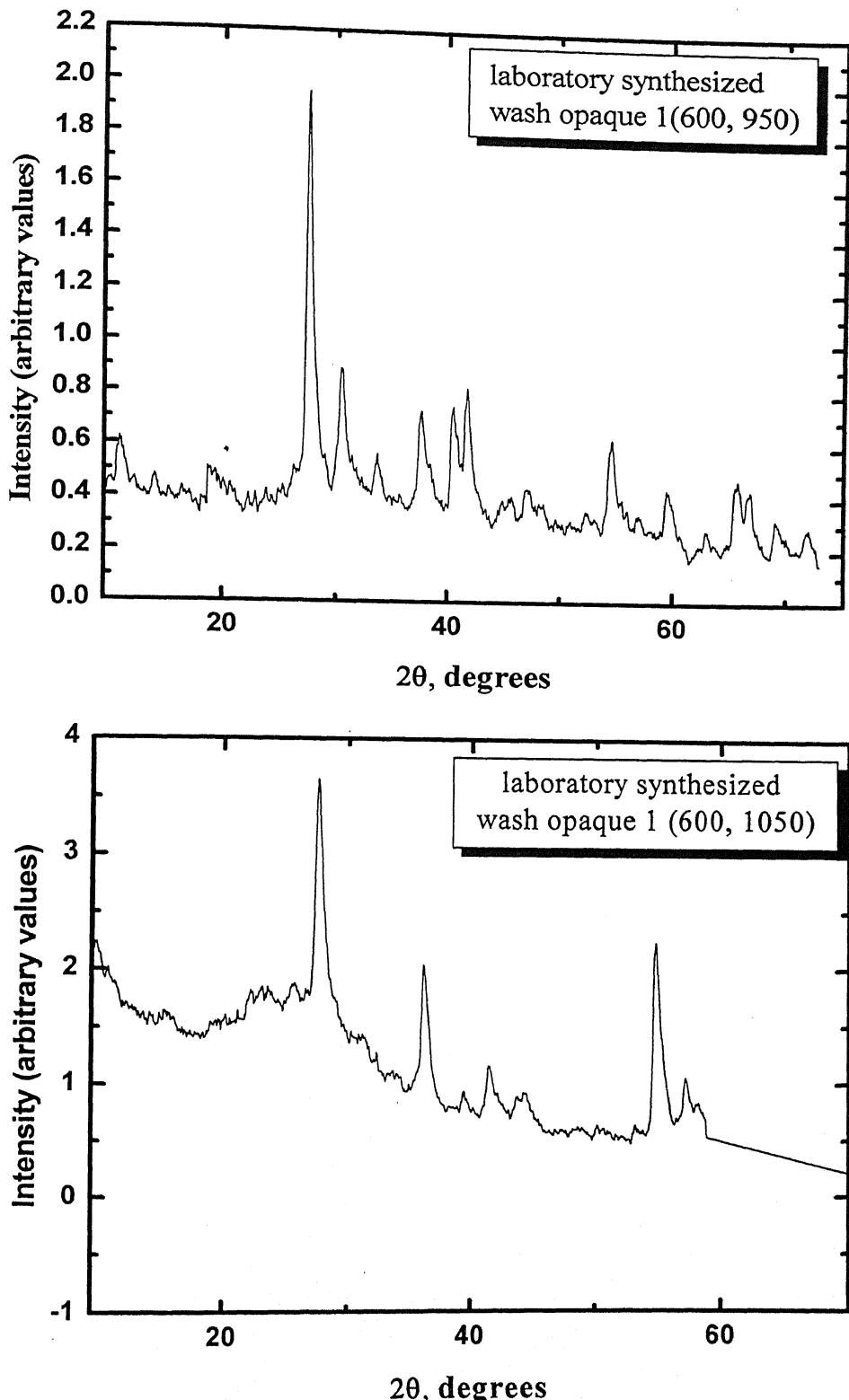


Fig. 4.5: XRD plots of laboratory synthesized wash opaque 1 at nucleation temperature 600°C (holding time 1hr) and crystallization at 750°C and 850°C (holding time in each case 1 hr).



**Fig. 4.6:** XRD plots of laboratory synthesized wash opaque 1 at nucleation temperature 600°C (holding time 1hr) and crystallization at 950°C and 1050°C (holding time in each case 1 hr).

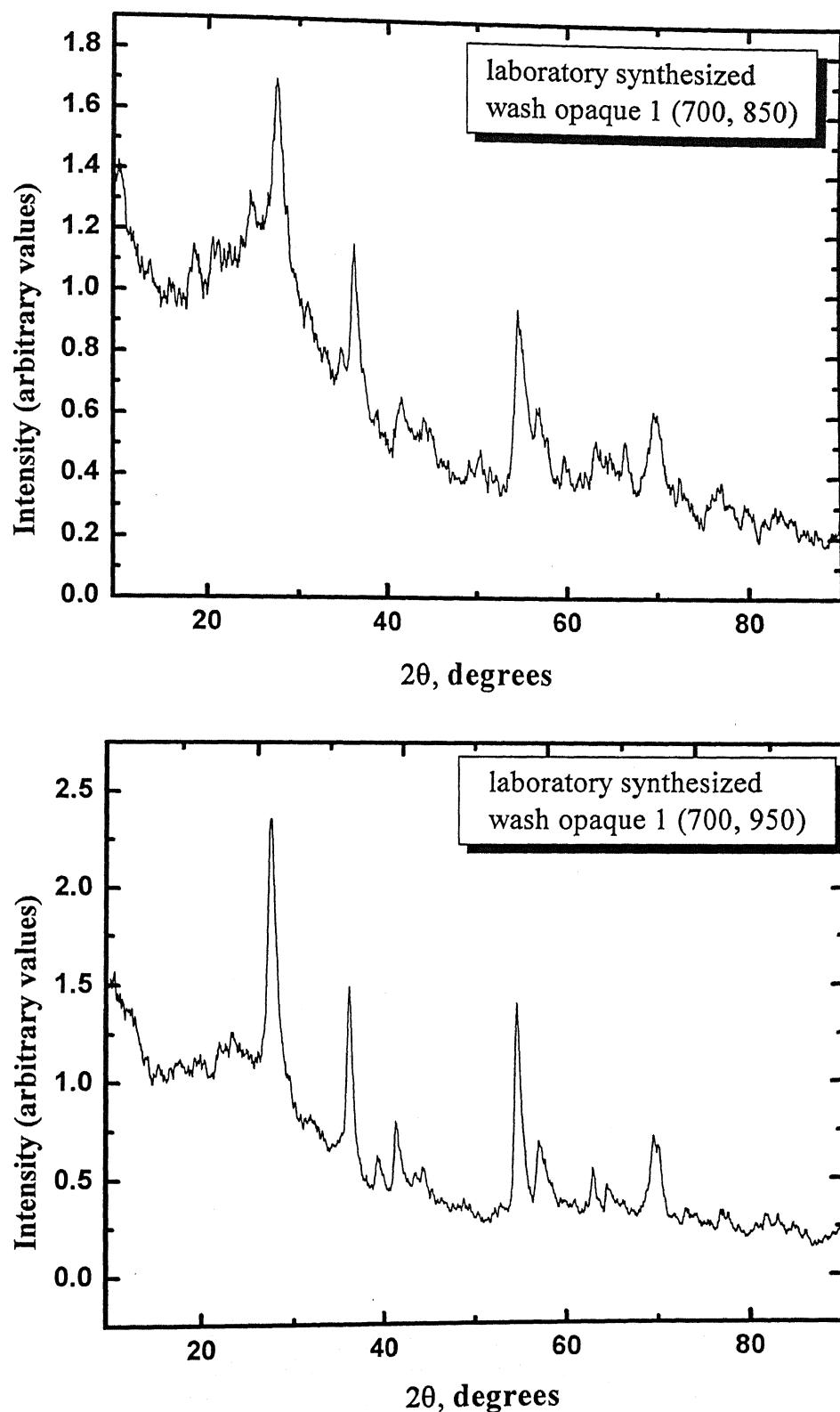
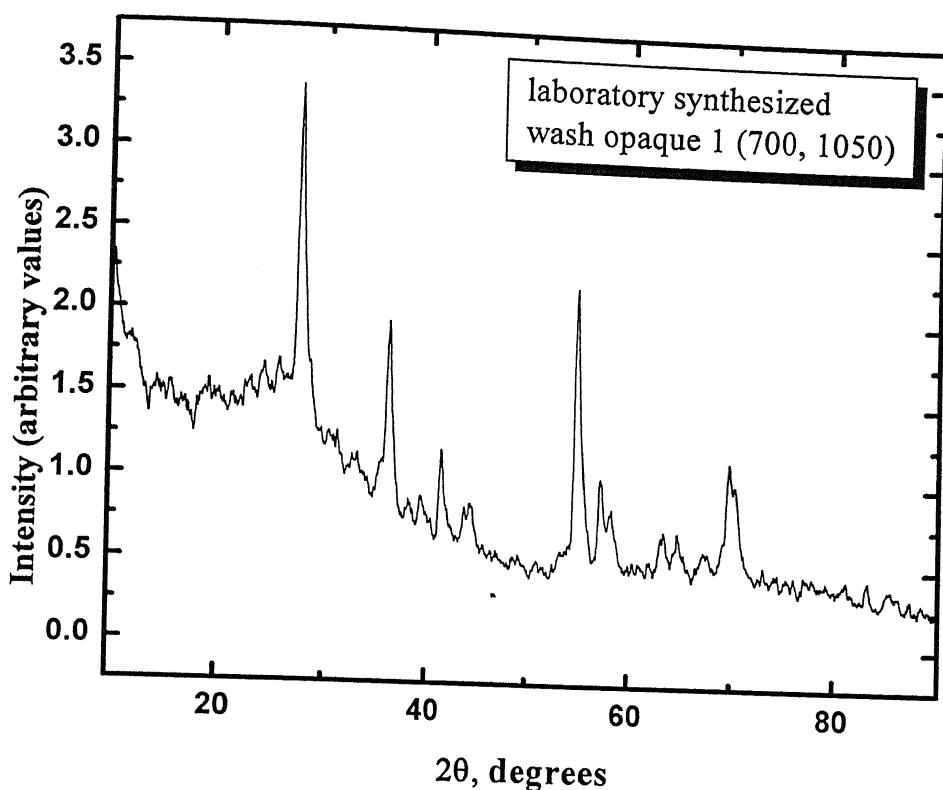


Fig. 4.7: XRD plots of laboratory synthesized wash opaque 1 at nucleation temperature 700°C (holding time 1hr) and crystallization at 850°C and 950°C (holding time in each case 1 hr).



**Fig. 4.8:** XRD plot of laboratory synthesized wash opaque 1 at nucleation temperature 700°C (holding time 1hr) and crystallization at 1050°C (holding time 1 hr).

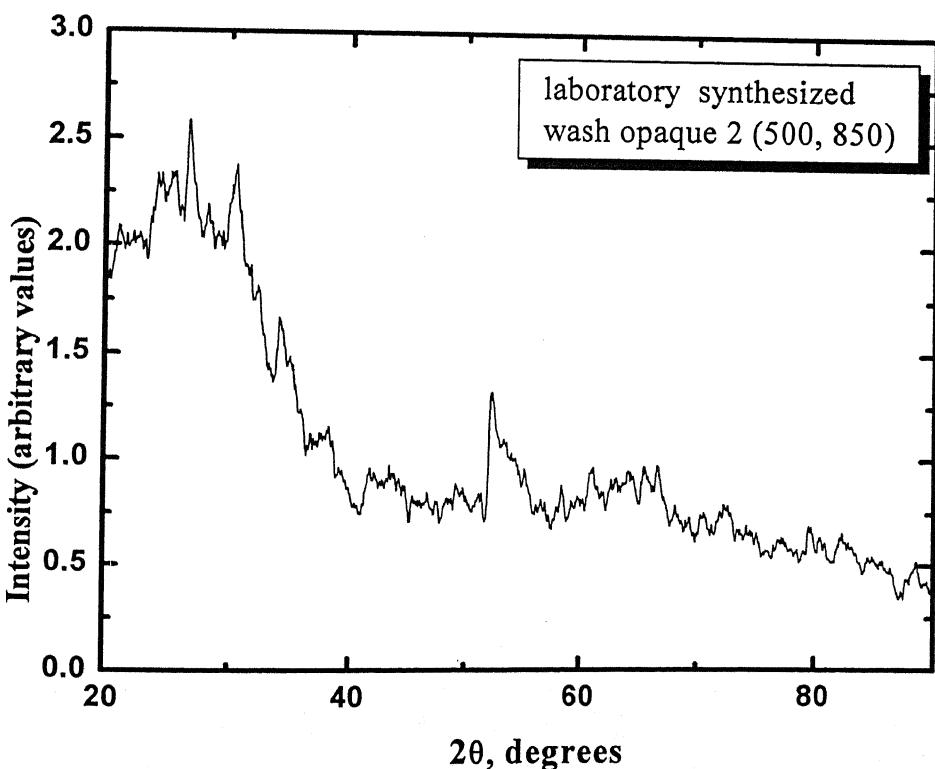
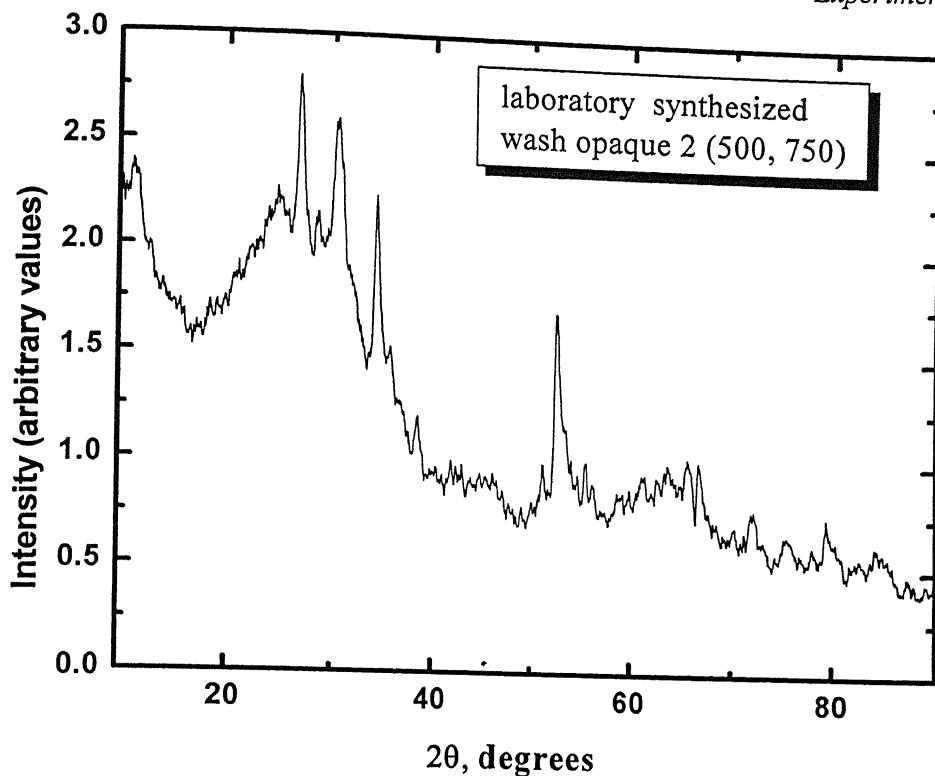
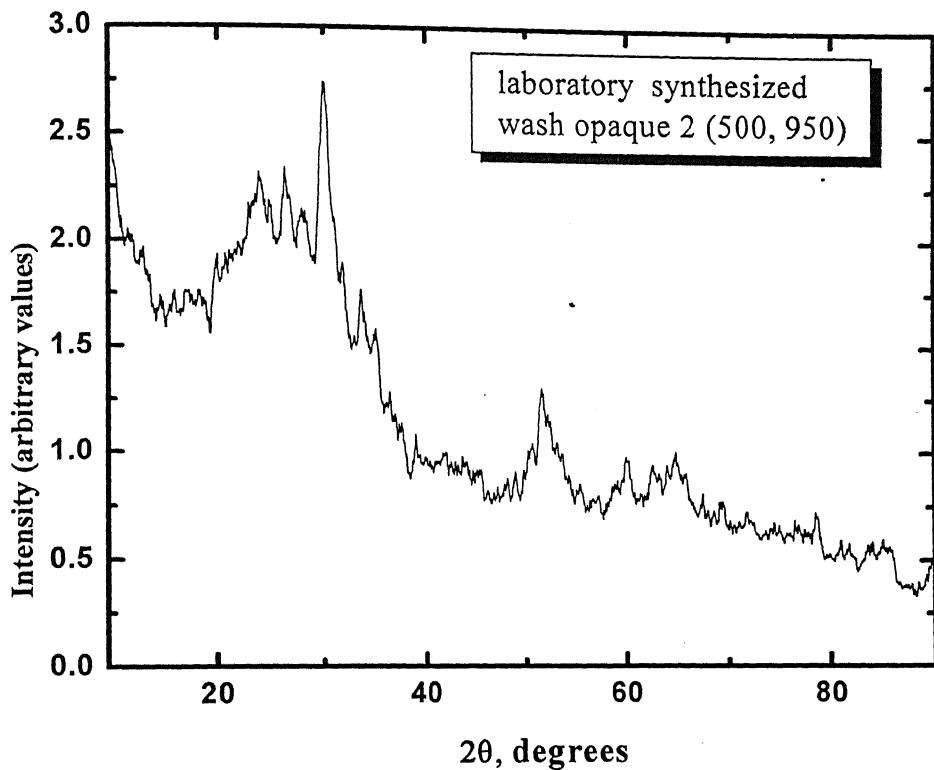


Fig. 4.9: XRD plots of laboratory synthesized wash opaque 2 at nucleation temperature 500°C (holding time 1hr) and crystallization at 750°C and 850°C (holding time in each case 1 hr).



**Fig. 4.10:** XRD plot of laboratory synthesized wash opaque 2 at nucleation temperature 500°C (holding time 1hr) and crystallization at 950°C (holding time 1 hr).

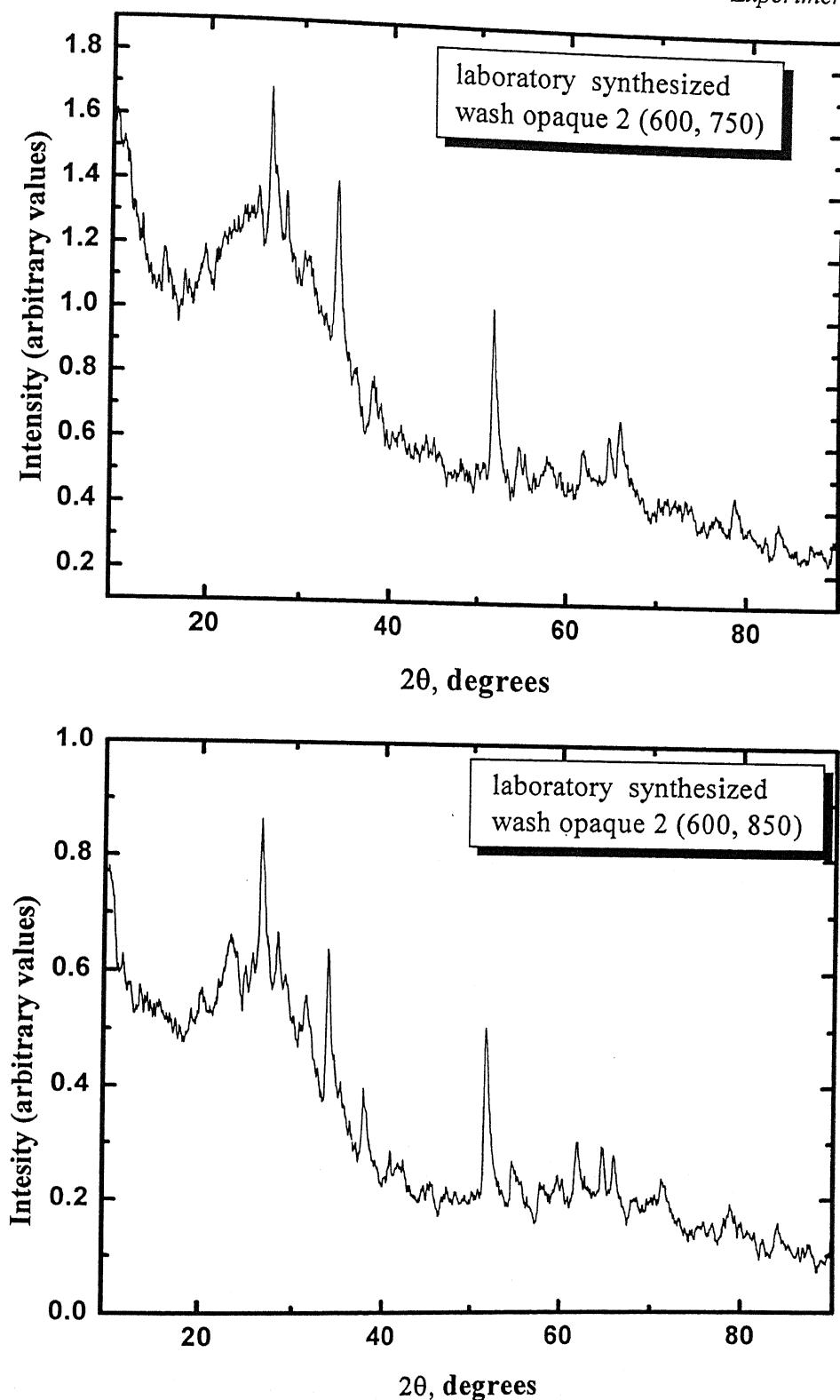
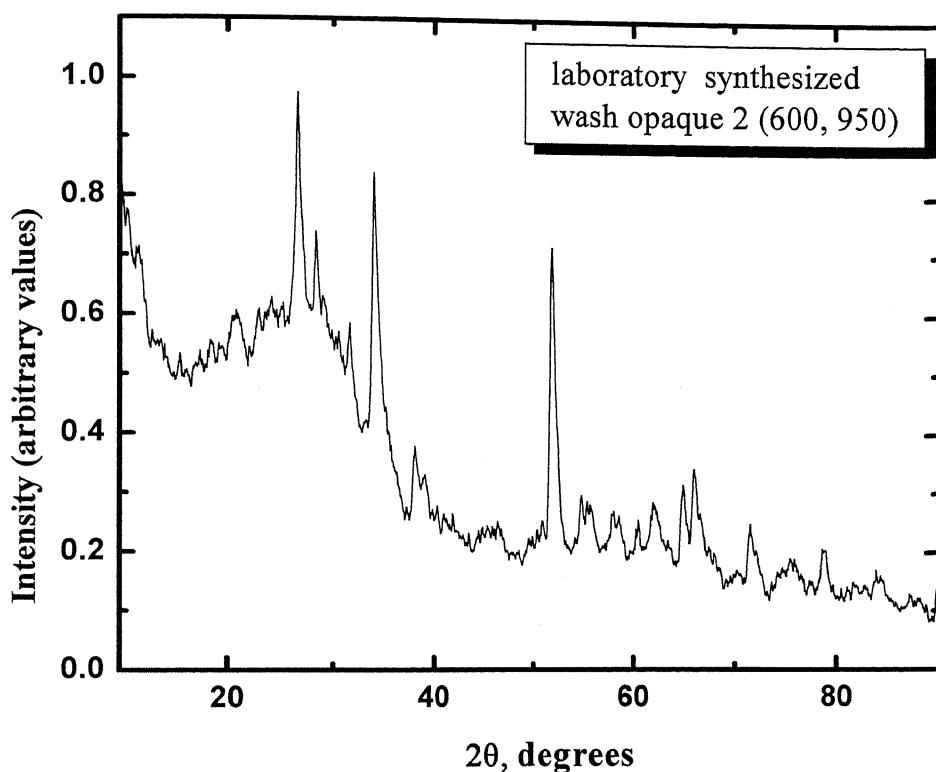


Fig. 4.11: XRD plots of laboratory synthesized wash opaque 2 at nucleation temperature 600°C (holding time 1hr) and crystallization at 750°C and 850°C (holding time 1 hr).



**Fig. 4.12:** XRD plot of laboratory synthesized wash opaque 2 at nucleation temperature 600°C (holding time 1hr) and crystallization at 950°C (holding time 1 hr).

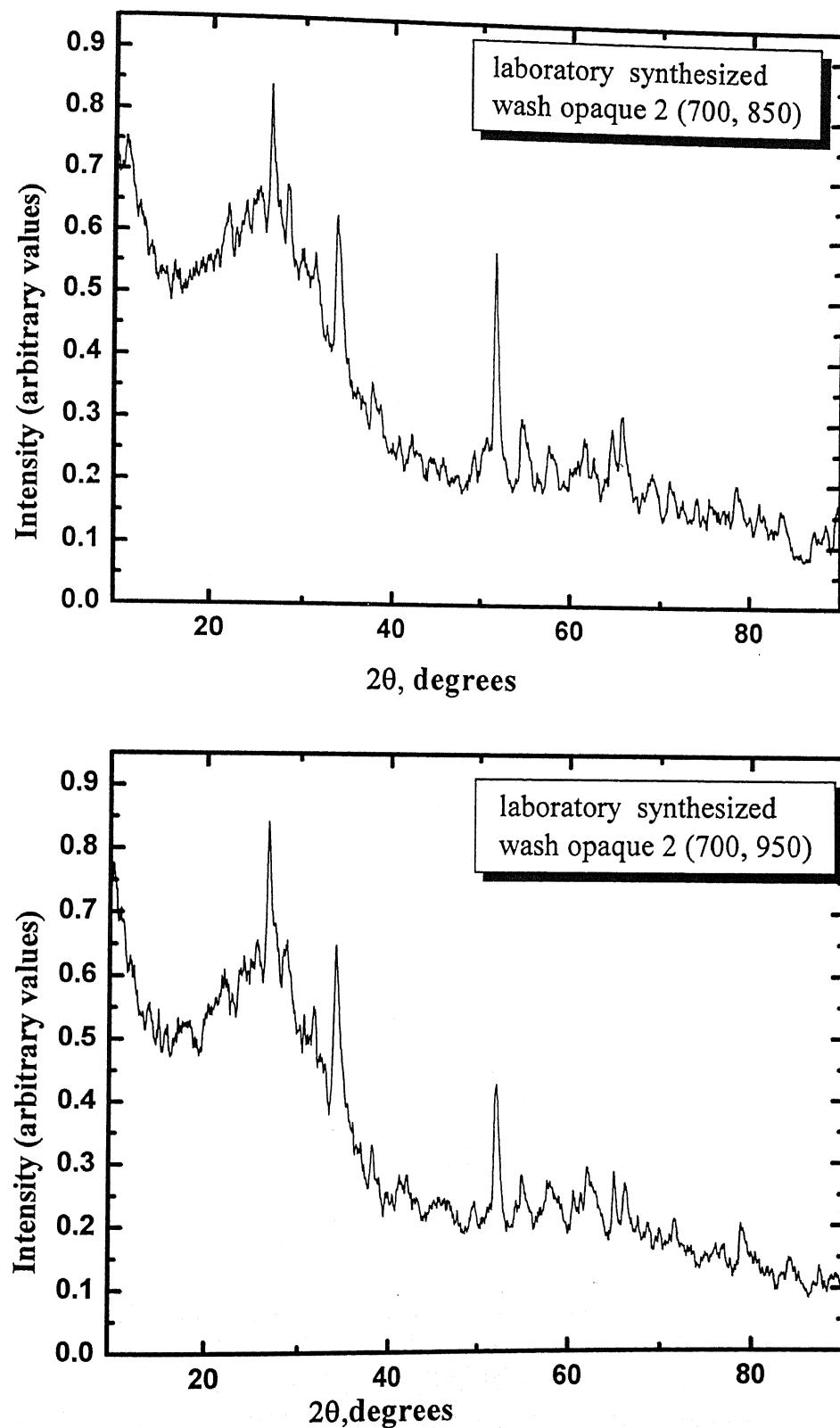


Fig. 4.13: XRD plots of laboratory synthesized wash opaque 2 at nucleation temperature  $700^\circ\text{C}$  (holding time 1 hr) and crystallization at  $850^\circ\text{C}$  and  $950^\circ\text{C}$  (holding time 1 hr).

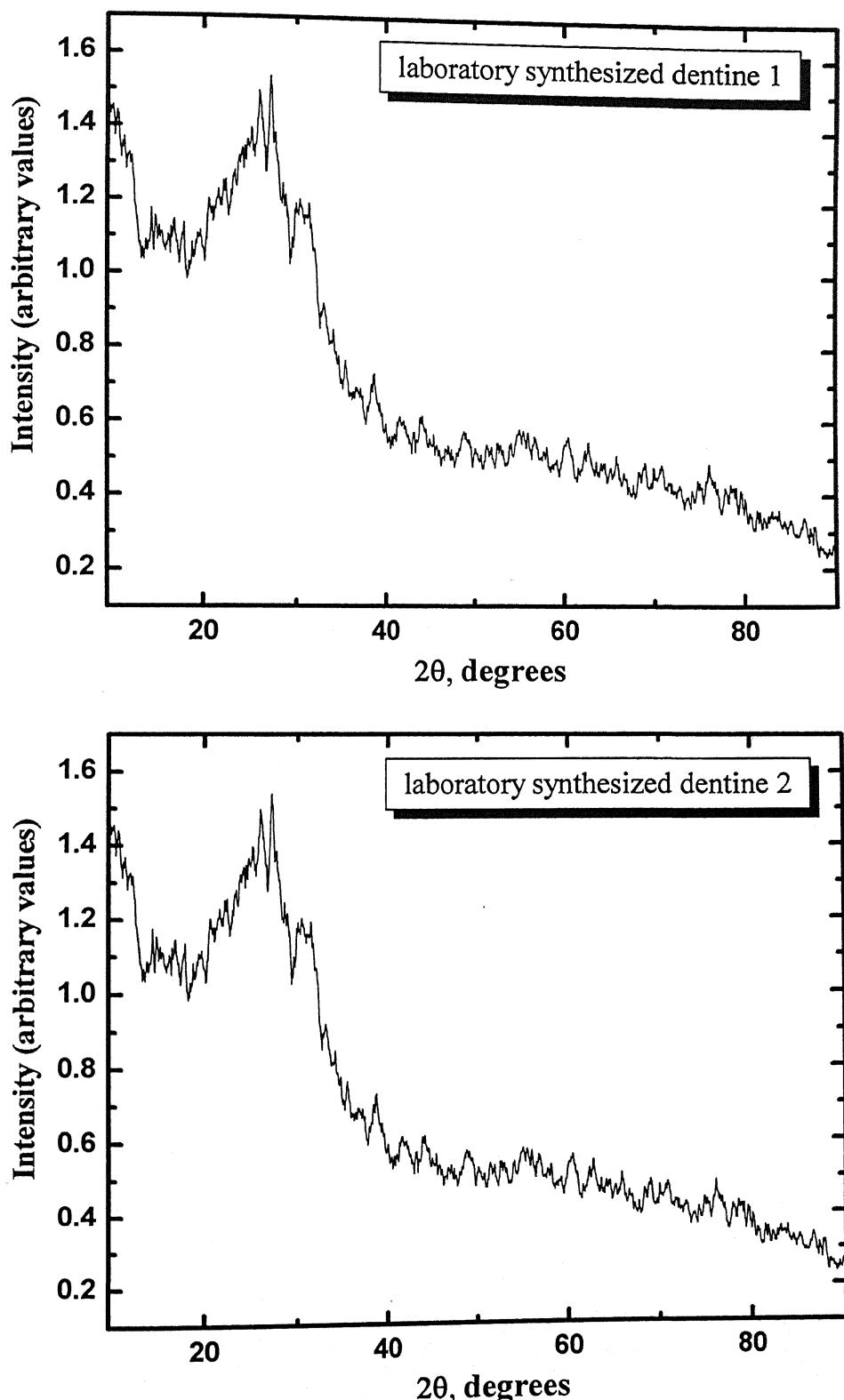


Fig 4.14: XRD plots of laboratory synthesized dentine 1 and 2

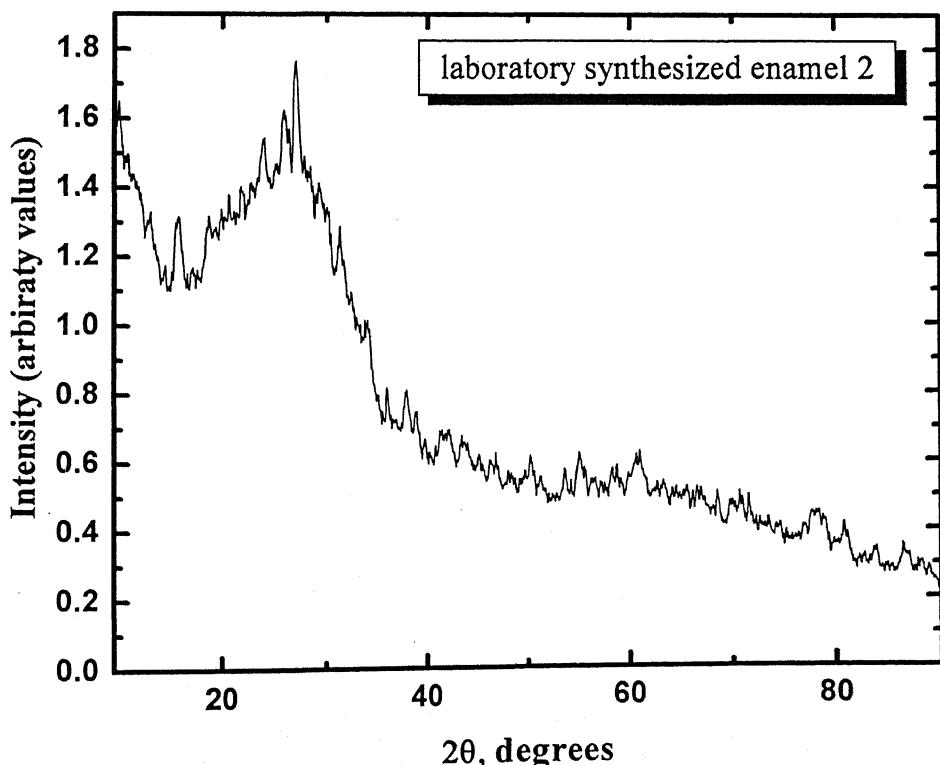
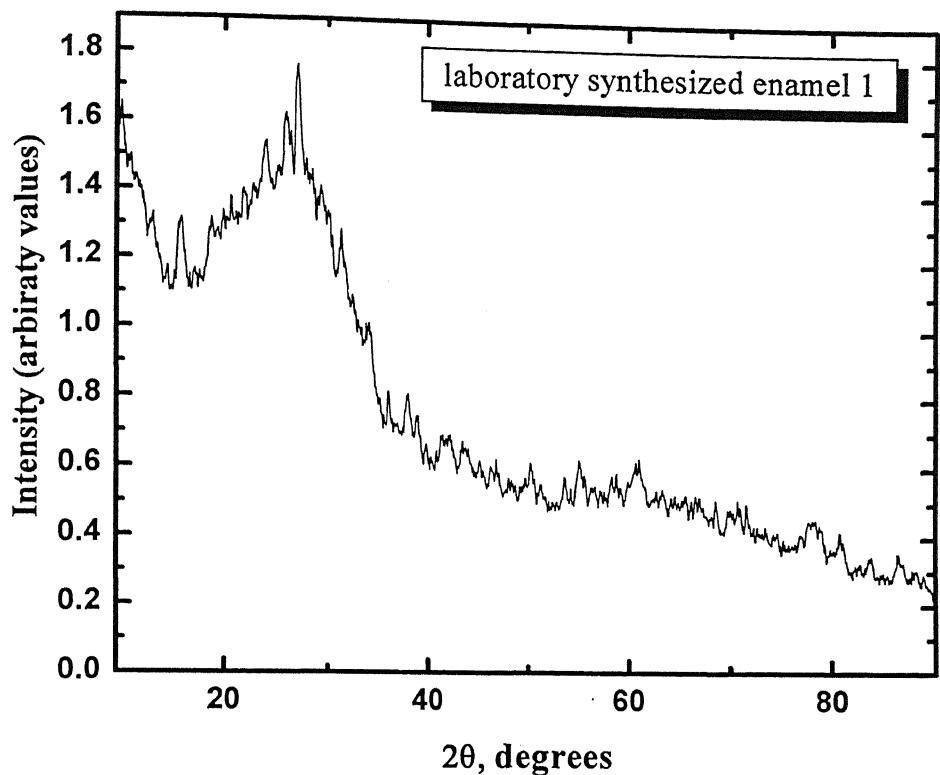


Fig. 4.15: XRD plots of laboratory synthesized enamel 1 and 2.

### **4.3 Particle size analysis results**

Fig. 4.16, 4.17 and 4.18 show the monomodal particle size distributions of the as received wash opaque, dentine and enamel. The particle size distribution plots for laboratory synthesized wash opaque 1 and 2 is given in Fig. 4.19. Similarly, particle size distribution curves for laboratory synthesized dentine 1 & 2 and enamel 1 & 2 are given in Fig. 4.20 and 4.21 respectively. These results have been critically discussed in Chapter 5.

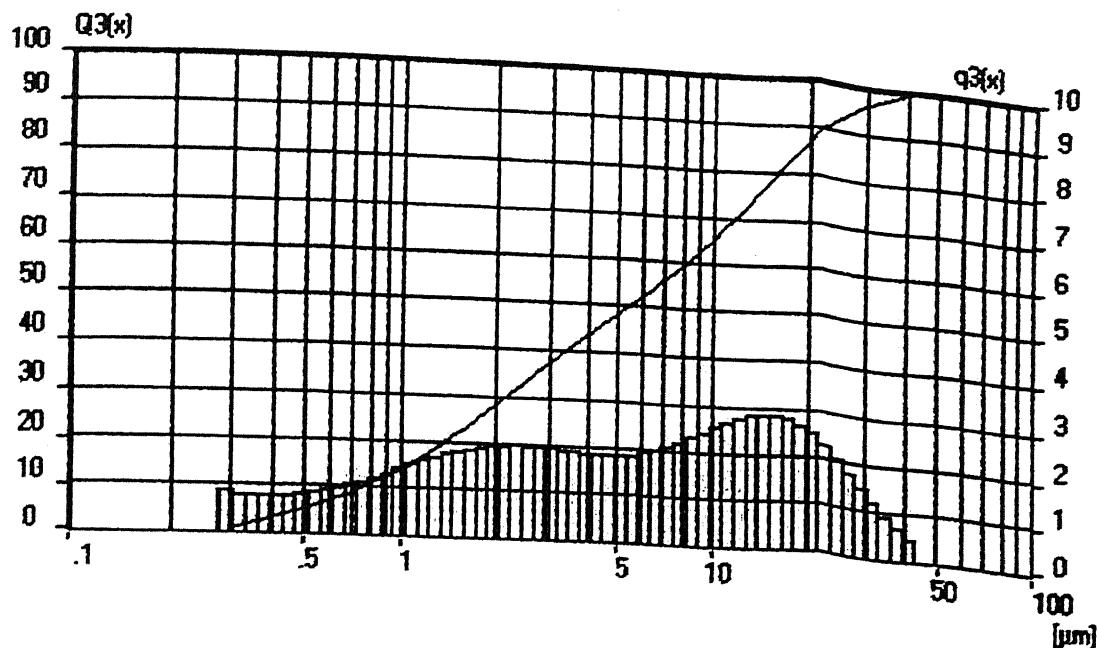


Fig. 4.16: Particle size distribution of as received wash opaque.

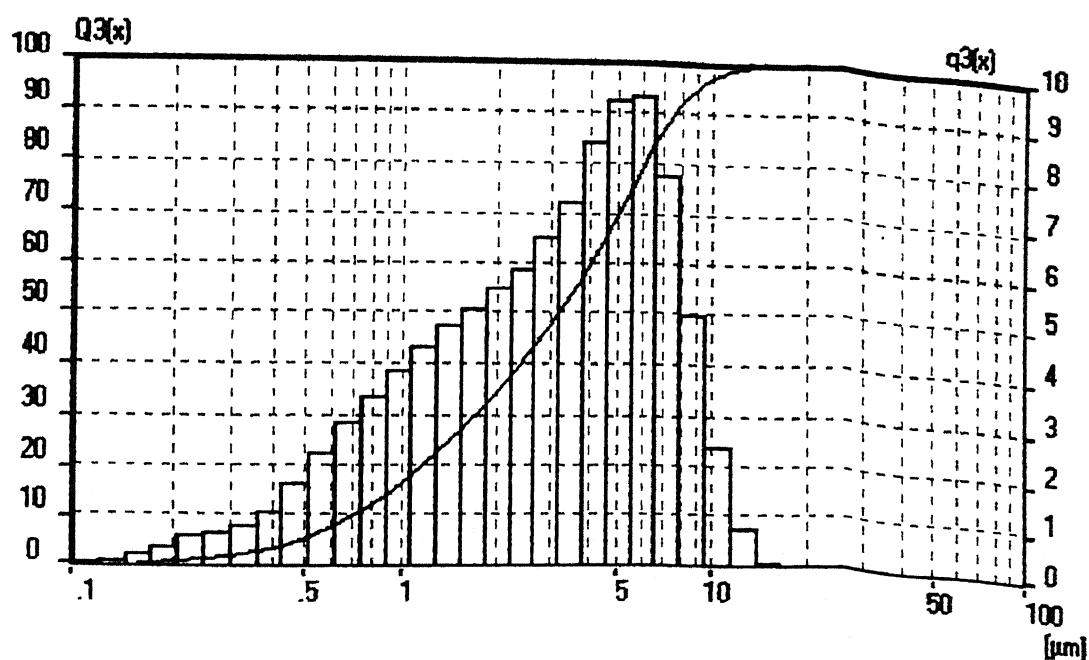


Fig. 4.17: Particle size distribution of as received dentine.

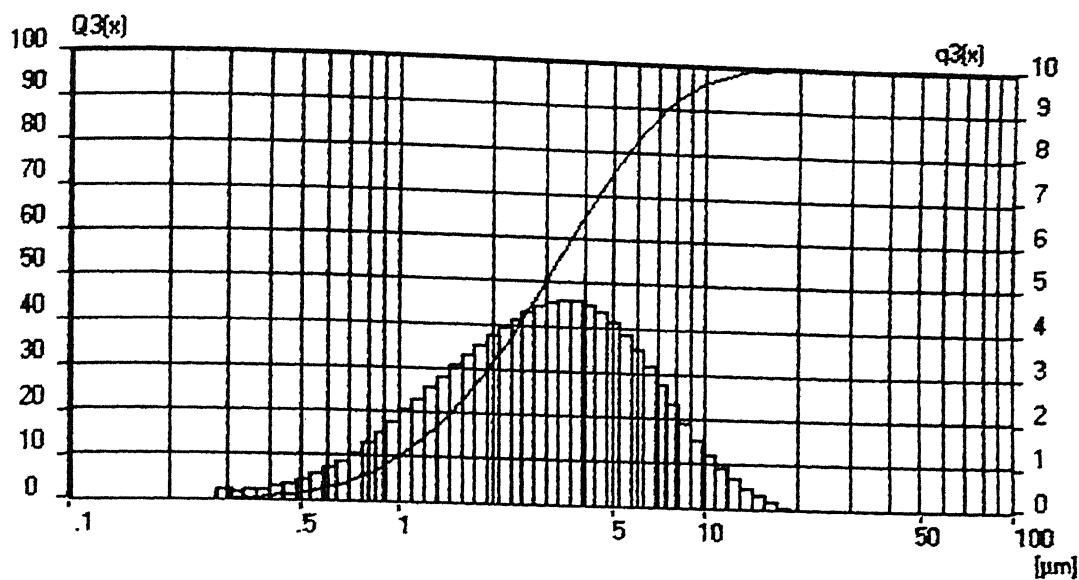


Fig. 4.18: Particle size distribution of as received enamel.

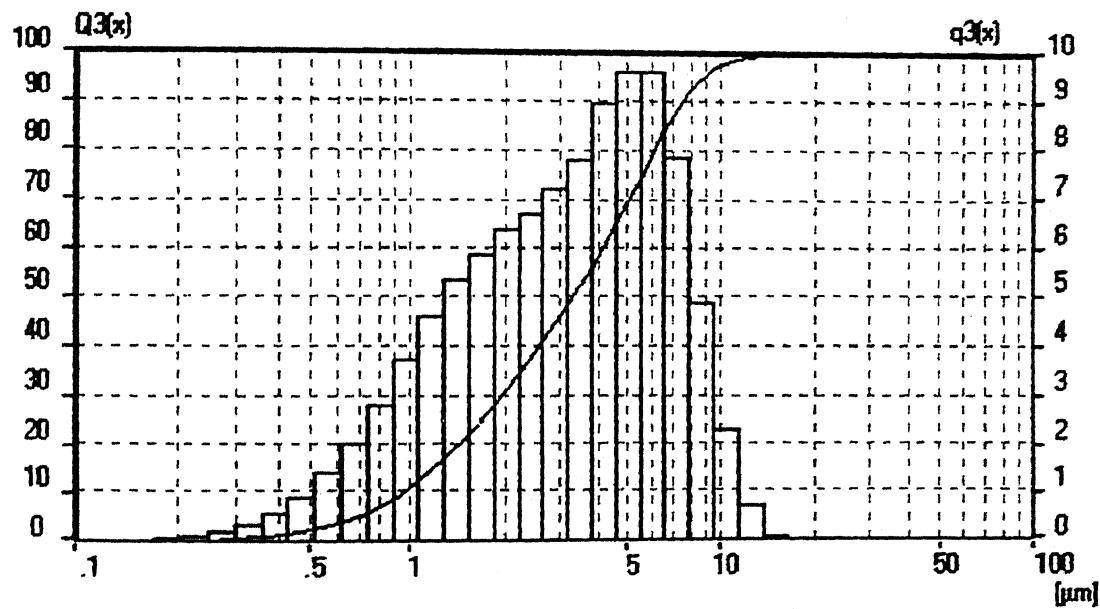


Fig. 4.19: Particle size distribution for laboratory synthesized wash opaque 1 and 2.

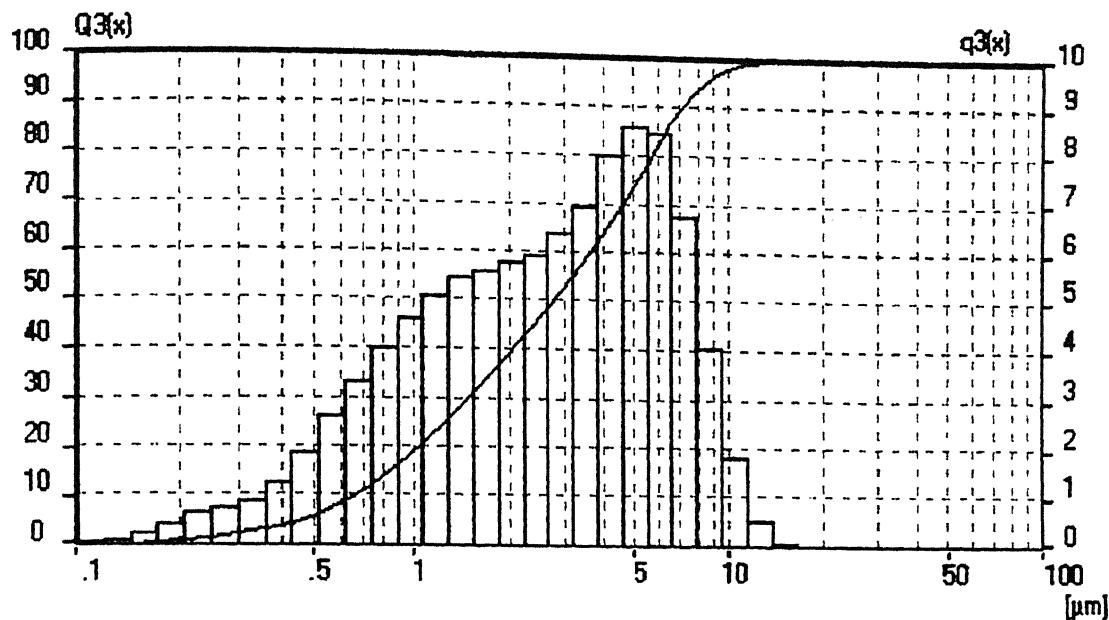


Fig. 4.20: Particle size distribution for laboratory synthesized dentine 1 and 2.

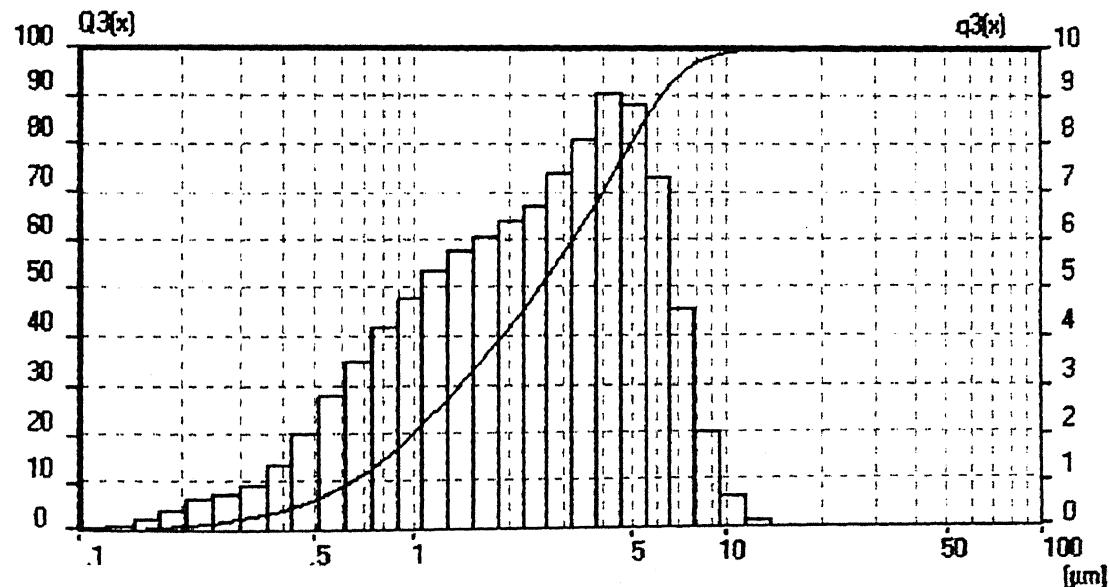


Fig. 4.21: Particle size distribution for laboratory synthesized enamel 1 and 2.

#### **4.4 TG/DTA results**

The TG/DTA plots for laboratory synthesized glass powders of wash opaque 1 and 2 are given in Fig. 4.22 and 4.23. From these graphs glass transition temperature and crystallization temperature during heat treatment were determined. These results have been critically discussed in Chapter 5.

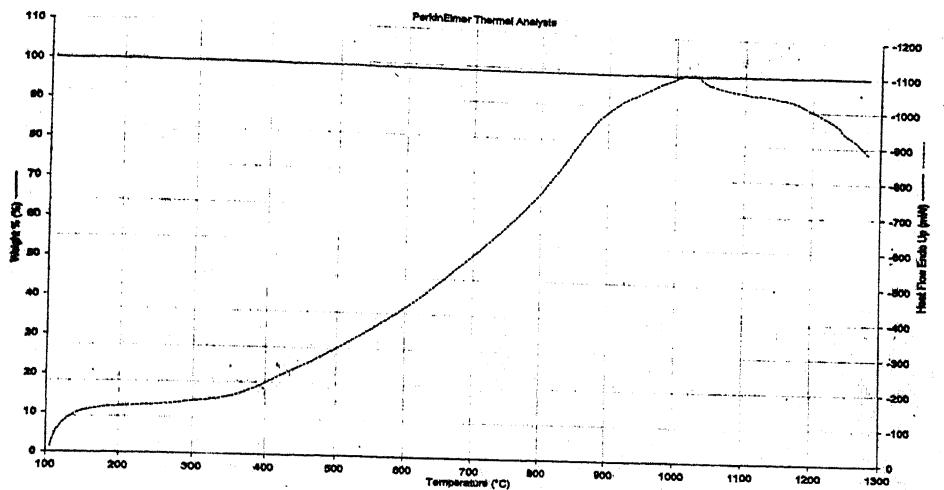


Fig. 4.22: TG/DTA curve for glass powder of laboratory synthesized wash opaque 1

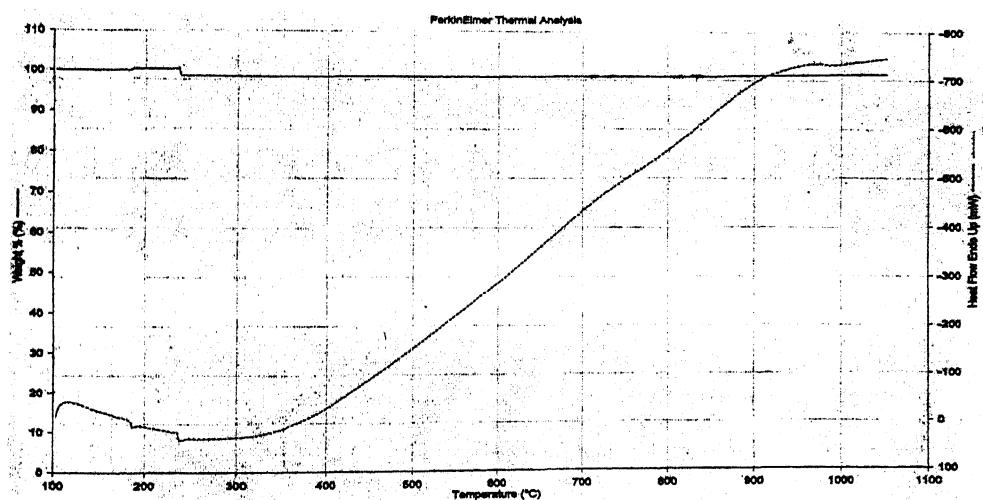
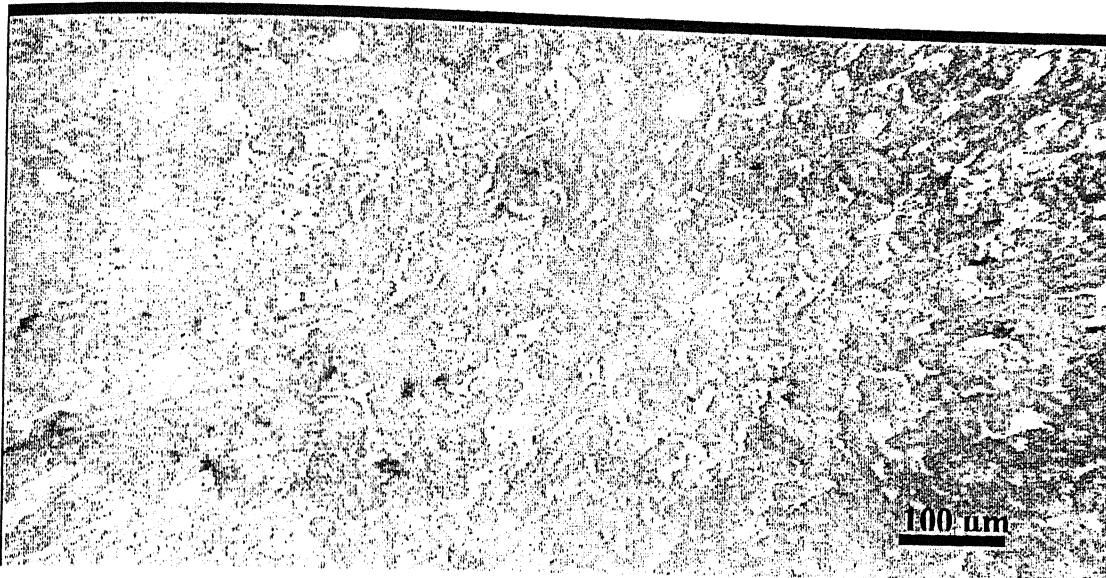


Fig. 4.23: TG/DTA curve for glass powder of laboratory synthesized wash opaque 2.

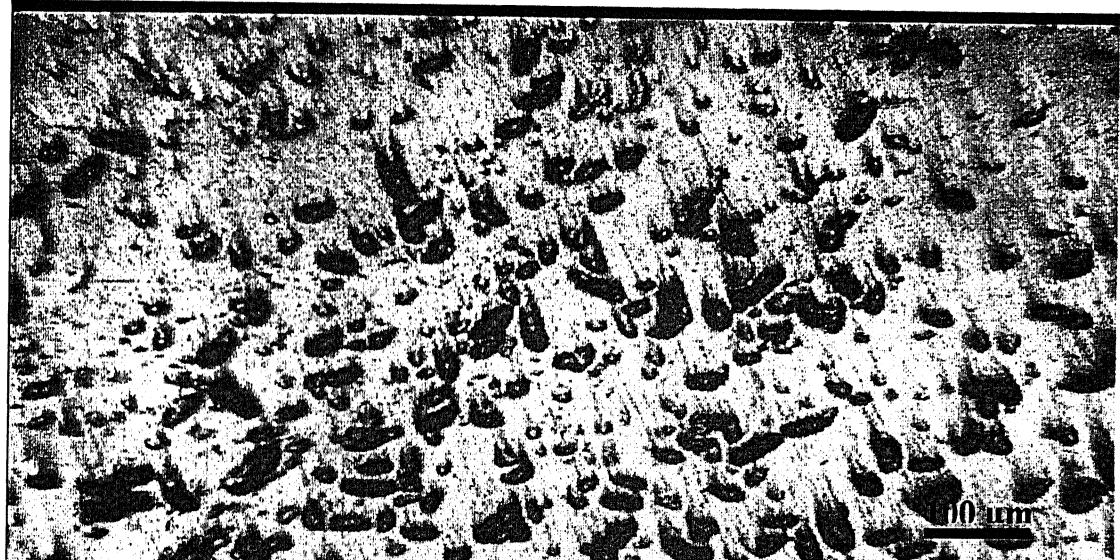
#### **4.5 Optical microscopy results**

Detailed optical microscopy of the synthesized wash opaque 1 and 2 have been carried out after the heat treatments which converted them into glass-ceramics. The extent and nature of the leucite crystals in the glassy matrix have been carefully studied. These results have been discussed critically in Chapter 5.

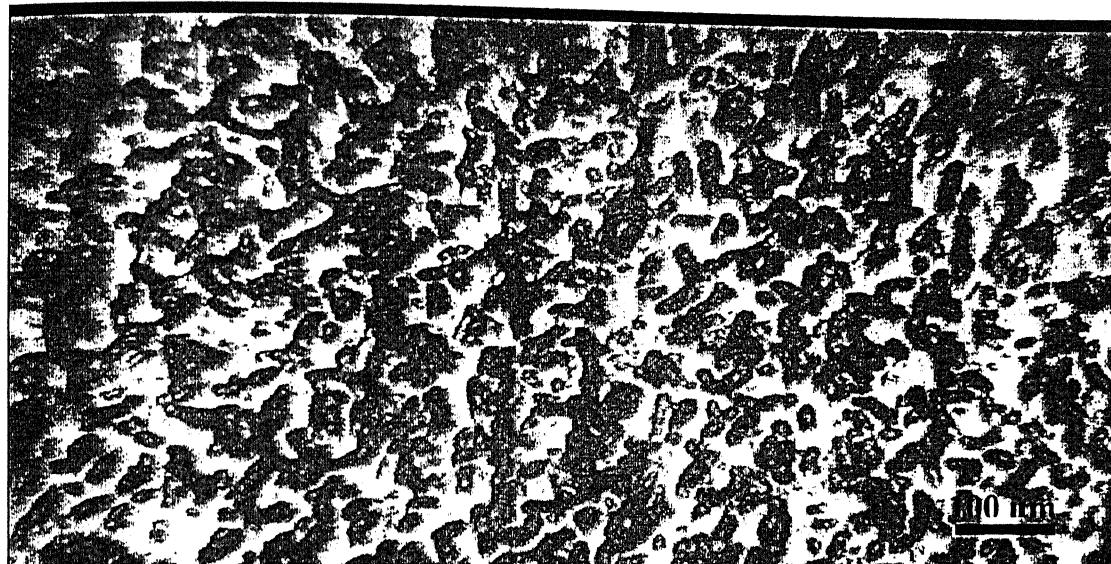
**Wash opaque 1**



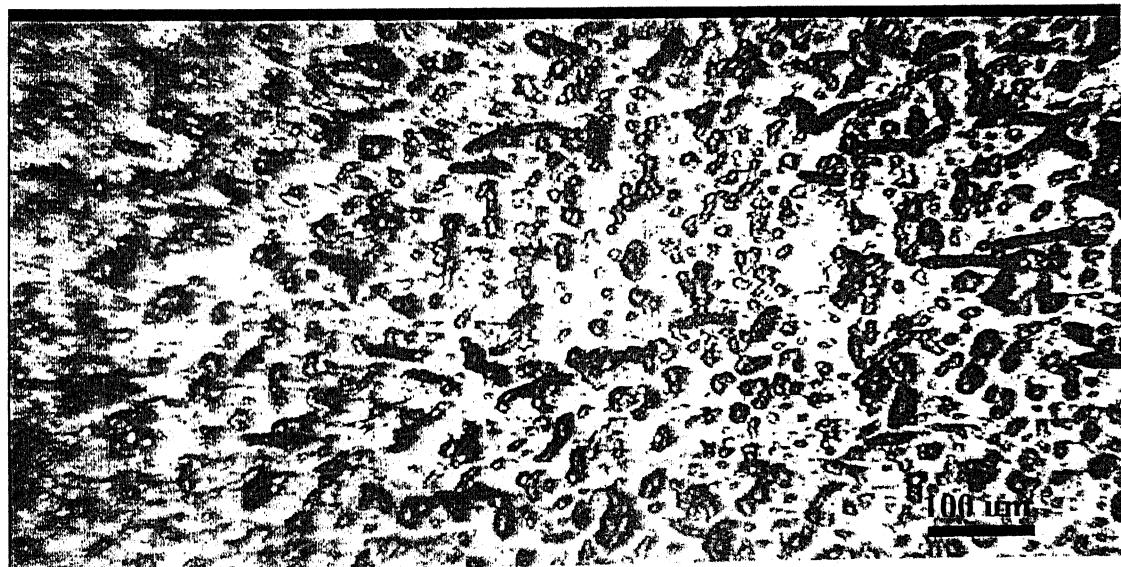
**Fig. 4.24:** Optical micrograph of wash opaque 1 at nucleation temperature of 500°C (holding temperature 1 hr) at 100 X magnification



**Fig. 4.25:** Optical micrograph of wash opaque 1 at nucleation temperature of 500°C (holding temperature 1 hr) and crystallization temperature of 750°C (holding temperature 1hr) at 100X magnification.

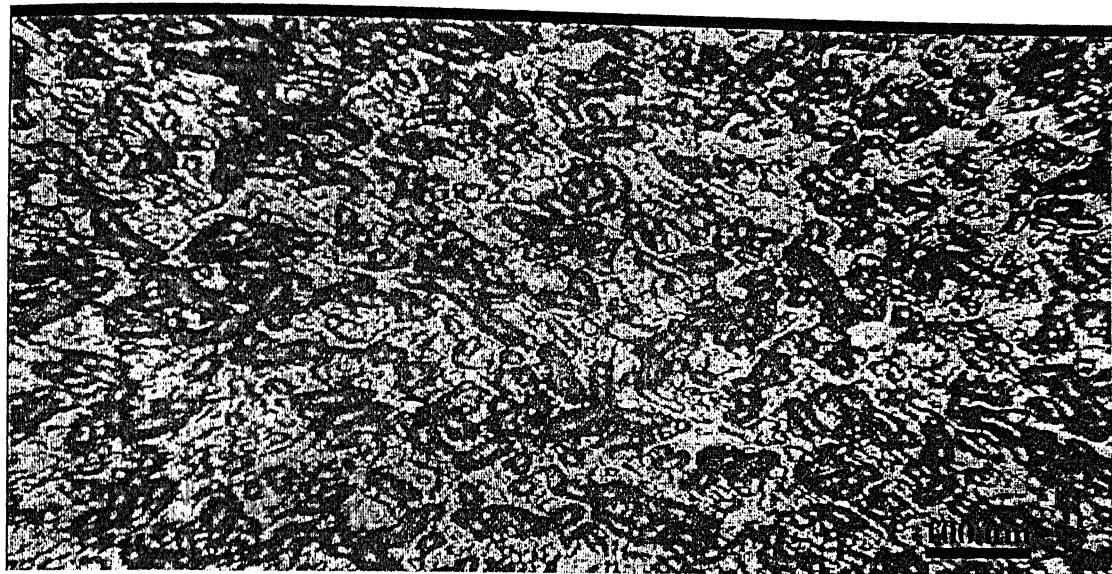


**Fig. 4.26:** Optical micrograph of wash opaque 1 at nucleation temperature of 500°C (holding temperature 1 hr) and crystallization temperature of 850°C (holding temperature 1hr) at 100X magnification.



**Fig. 4.27:** Optical micrograph of wash opaque 1 at nucleation temperature of 500°C (holding temperature 1 hr) and crystallization temperature of 950°C (holding temperature 1hr) at 100X magnification

## *Experimental Results*



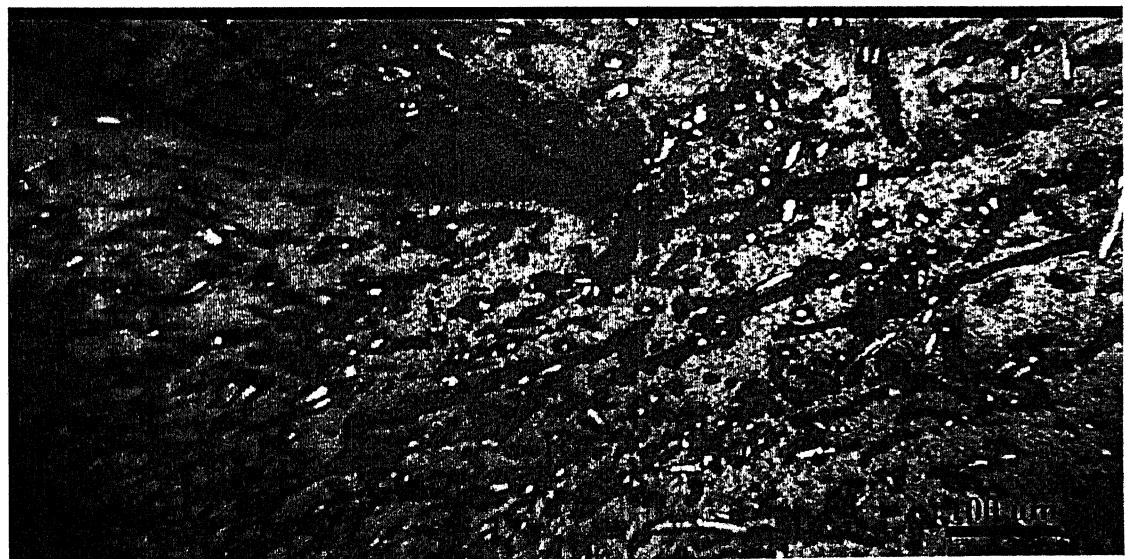
**Fig. 4.28:** Optical micrograph of wash opaque 1 at nucleation temperature of 500°C (holding temperature 1 hr) and crystallization temperature of 1050°C (holding temperature 1hr) at 100X magnification.



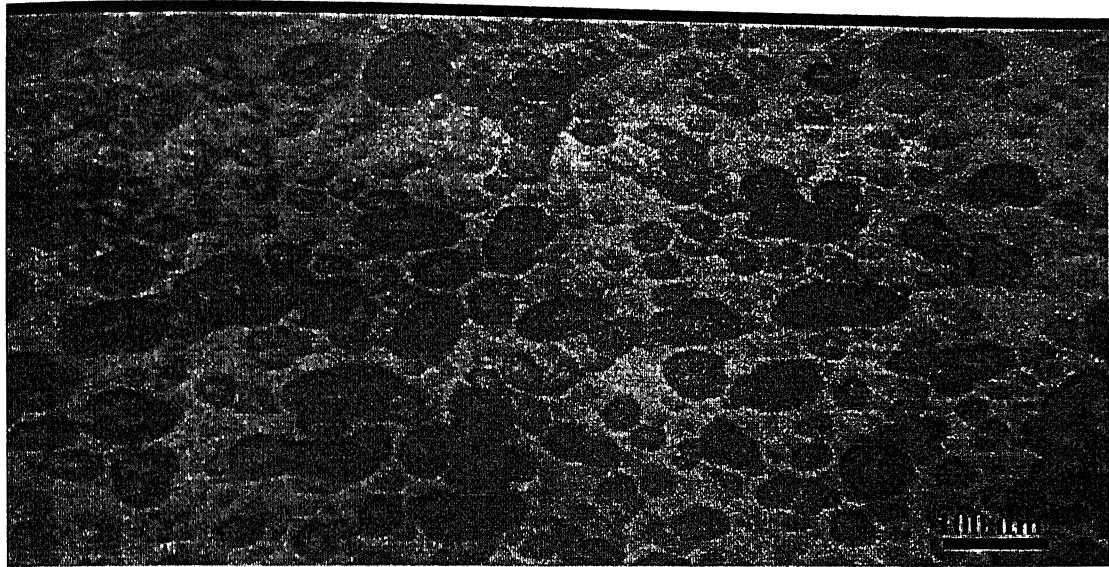
**Fig. 4.29:** Optical micrograph of laboratory synthesized wash opaque 1 at nucleation temperature of 600°C (holding temperature 1 hr) at 100 X magnification.



**Fig. 4.30:** Optical micrograph of laboratory synthesized wash opaque 1 at nucleation temperature of 600°C (holding temperature 1 hr) and crystallization temperature of 750°C (holding temperature 1hr) at 100X magnification.



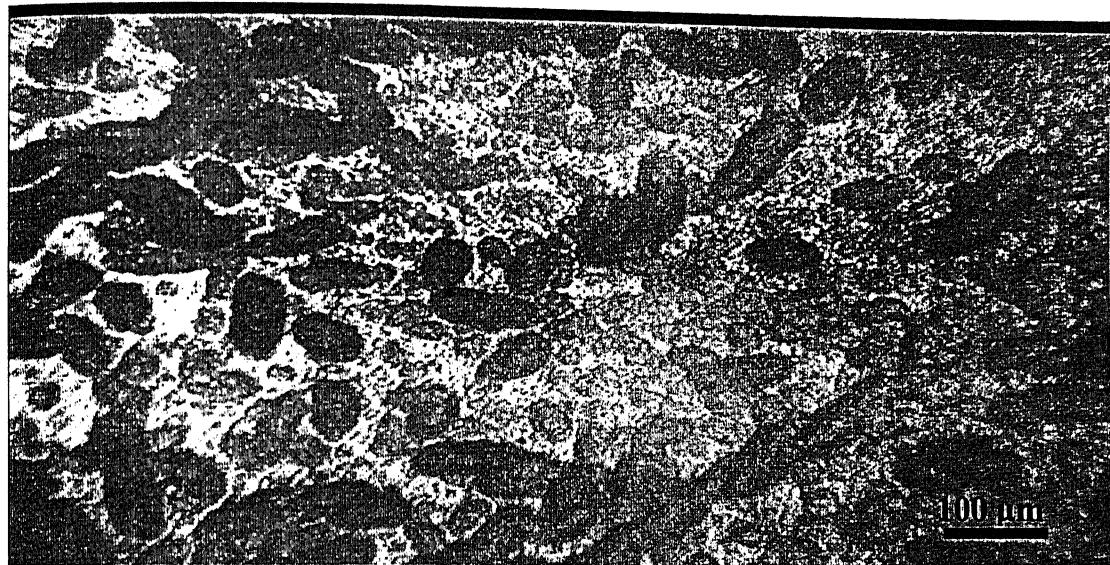
**Fig. 4.31:** Optical micrograph of laboratory synthesized wash opaque 1 at nucleation temperature of 600°C (holding temperature 1 hr) and crystallization temperature of 850°C (holding temperature 1hr) at 100X magnification.



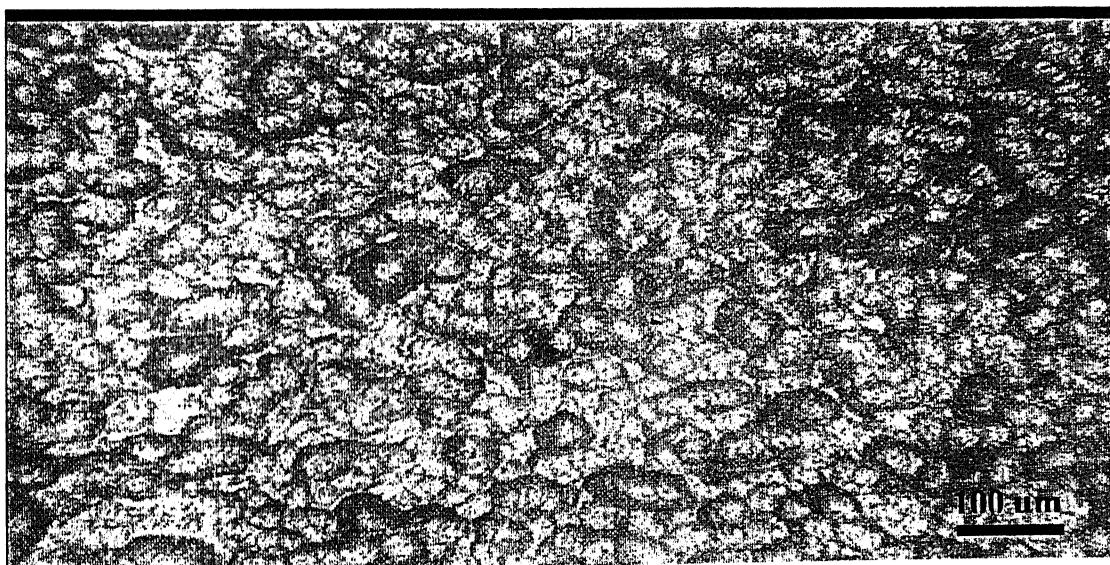
**Fig. 4.32:** Optical micrograph of laboratory synthesized wash opaque 1 at nucleation temperature of 600°C (holding temperature 1 hr) and crystallization temperature of 950°C (holding temperature 1hr) at 100X magnification.



**Fig. 4.33:** Optical micrograph of laboratory synthesized wash opaque 1 at nucleation temperature of 600°C (holding temperature 1 hr) and crystallization temperature of 1050°C (holding temperature 1hr) at 100X magnification.



**Fig. 4.34:** Optical micrograph of laboratory synthesized wash opaque 1 at nucleation temperature of 700°C (holding temperature 1 hr) at 100X magnification.



**Fig. 4.35:** Optical micrograph of laboratory synthesized wash opaque 1 at nucleation temperature of 700°C (holding temperature 1 hr) and crystallization temperature of 850°C (holding temperature 1hr) at 100X magnification.

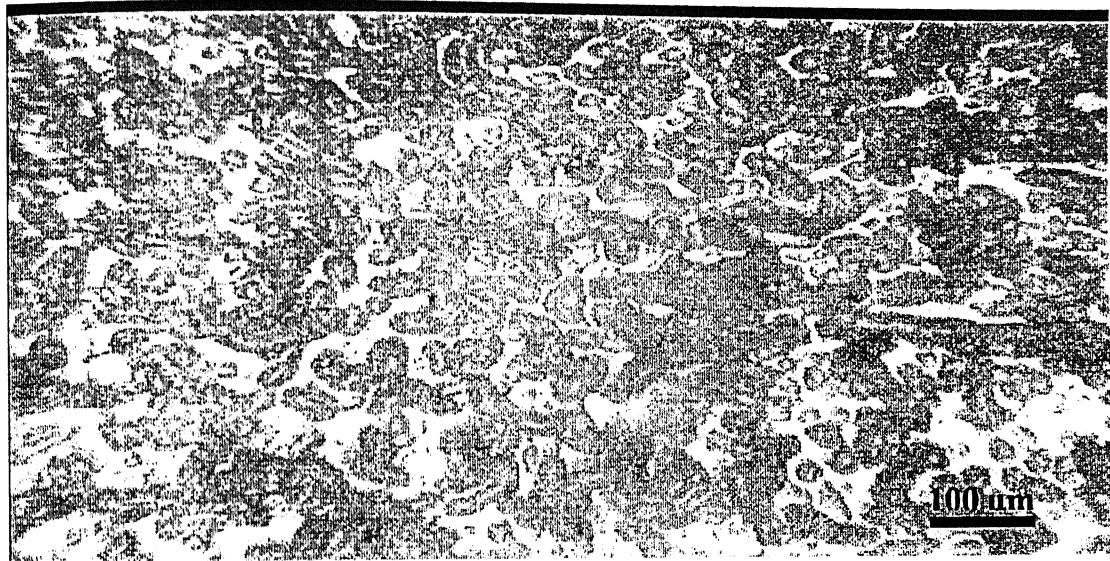


Fig. 4.36: Optical micrograph of laboratory synthesized wash opaque 1 at nucleation temperature of 700°C (holding temperature 1 hr) and crystallization temperature of 950°C (holding temperature 1hr) at 100X magnification.

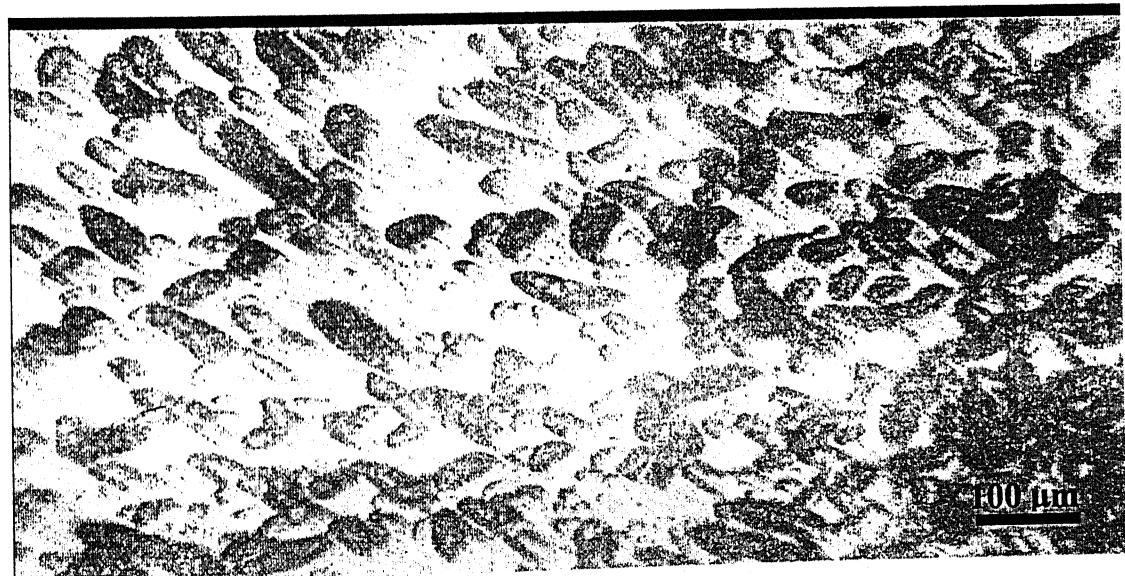


Fig. 4.37: Optical micrograph of laboratory synthesized wash opaque 1 at nucleation temperature of 700°C (holding temperature 1 hr) and crystallization temperature of 1050°C (holding temperature 1hr) at 100X magnification.

Wash opaque 2



Fig. 4.38: Optical micrograph of laboratory synthesized wash opaque 2 at nucleation temperature of 500°C (holding temperature 1 hr) at 100X magnification.

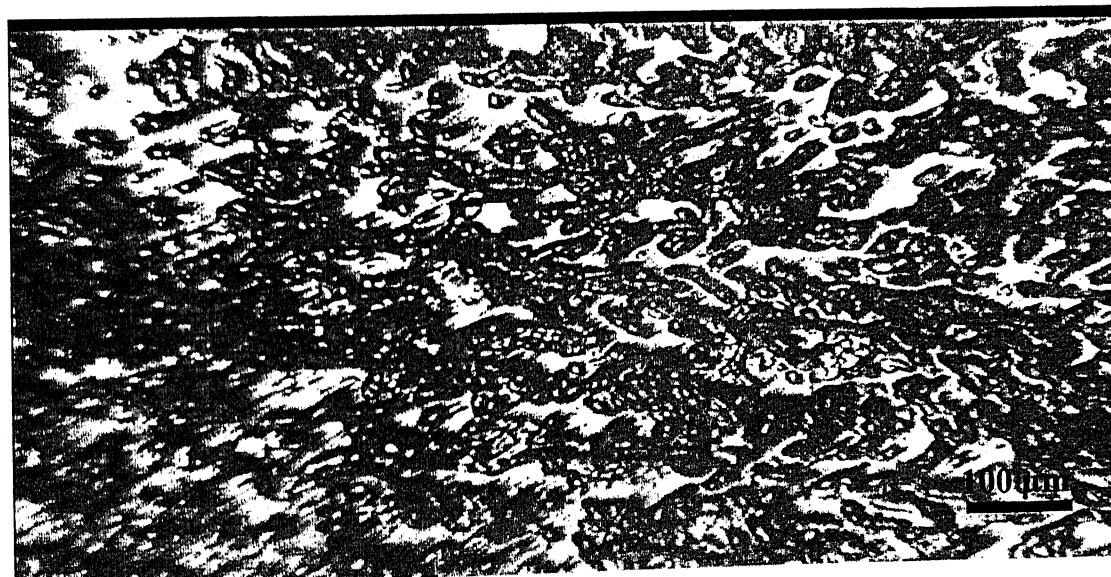


Fig. 4.39: Optical micrograph of laboratory synthesized wash opaque 2 at nucleation temperature of 500°C (holding temperature 1 hr) and crystallization temperature of 750°C (holding temperature 1hr) at 100X magnification.

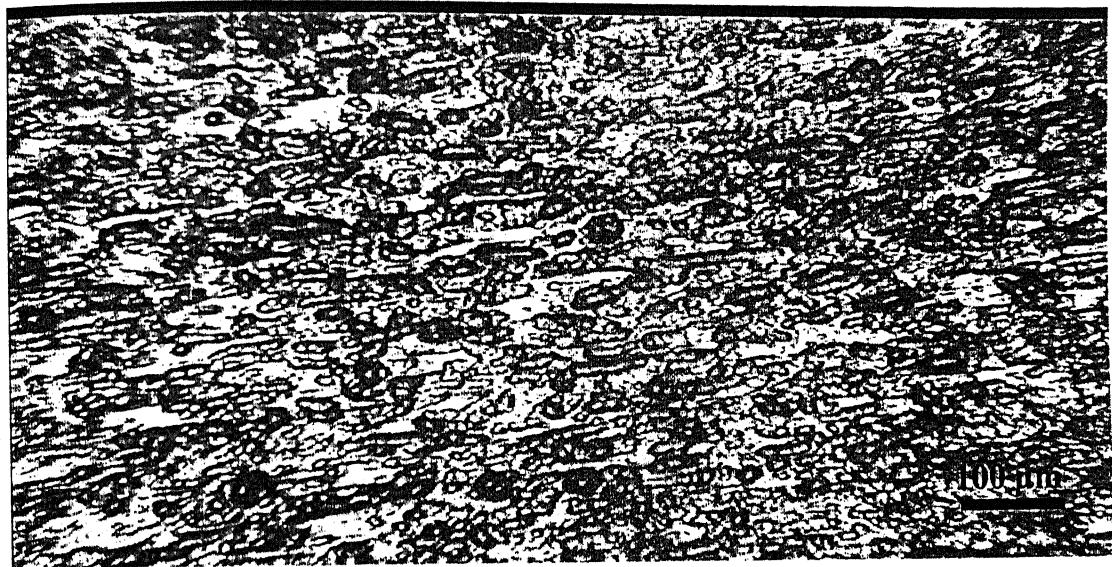


Fig. 4.40: Optical micrograph of laboratory synthesized wash opaque 2 at nucleation temperature of 500°C (holding temperature 1 hr) and crystallization temperature of 850°C (holding temperature 1hr) at 100X magnification.

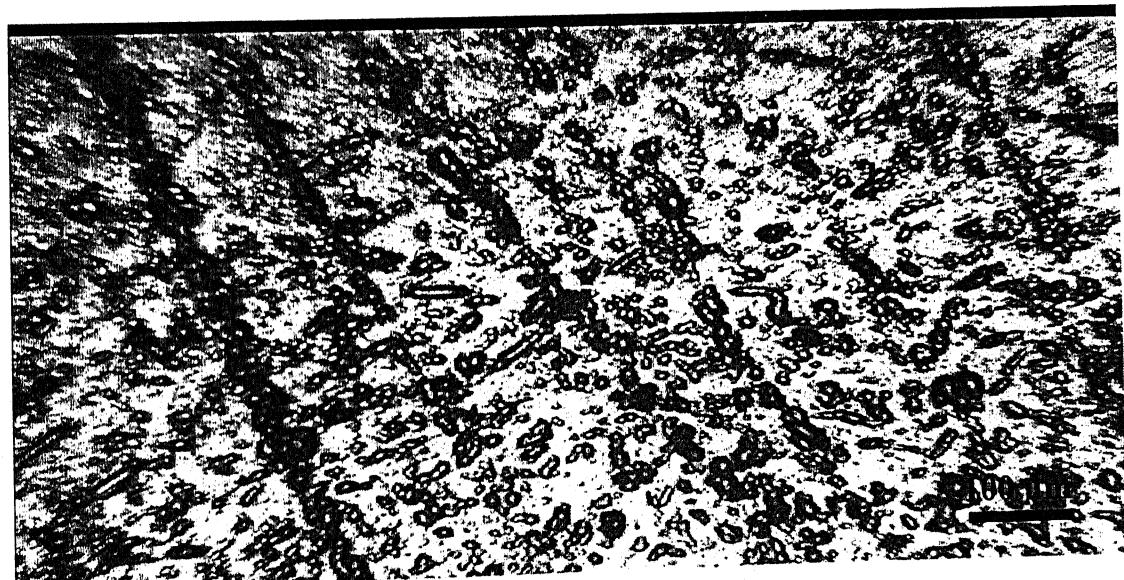


Fig. 4.41: Optical micrograph of laboratory synthesized wash opaque 2 at nucleation temperature of 500°C (holding temperature 1 hr) and crystallization temperature of 950°C (holding temperature 1hr) at 100X magnification.

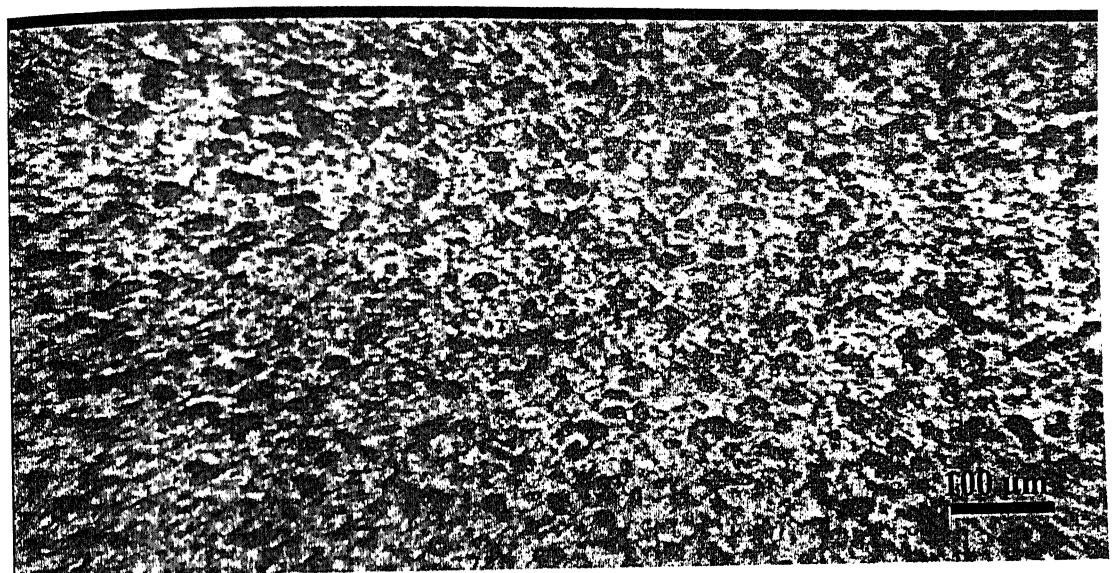


Fig. 4.42: Optical micrograph of laboratory synthesized wash opaque 2 at nucleation temperature of 600°C (holding temperature 1 hr) at 100X magnification.

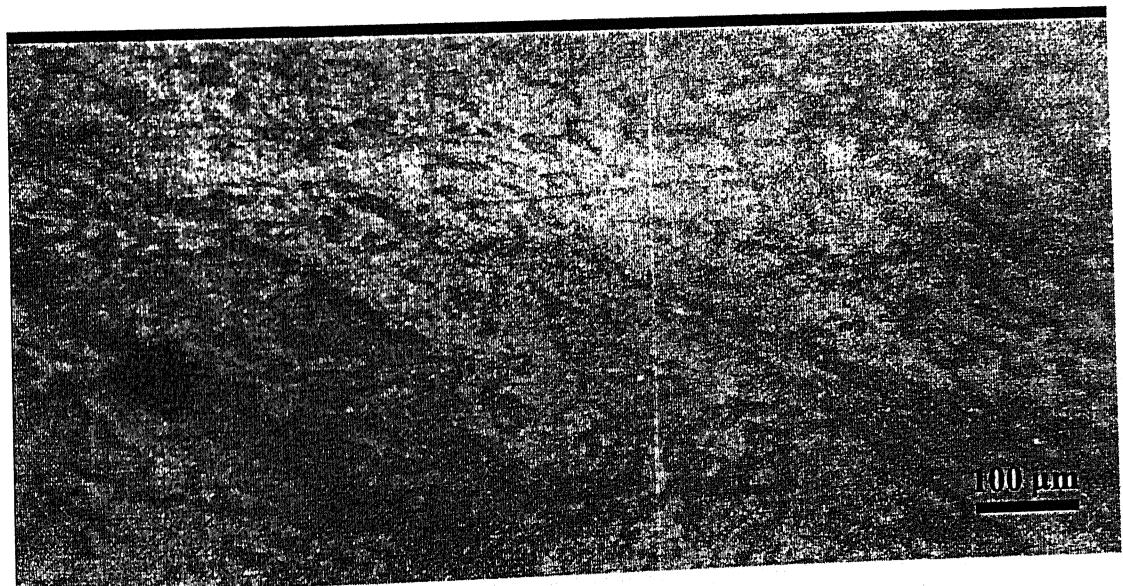


Fig. 4.43: Optical micrograph of laboratory synthesized wash opaque 2 at nucleation temperature of 600°C (holding temperature 1 hr) and crystallization temperature of 750°C (holding temperature 1hr) at 100X magnification.

## Experimental Results

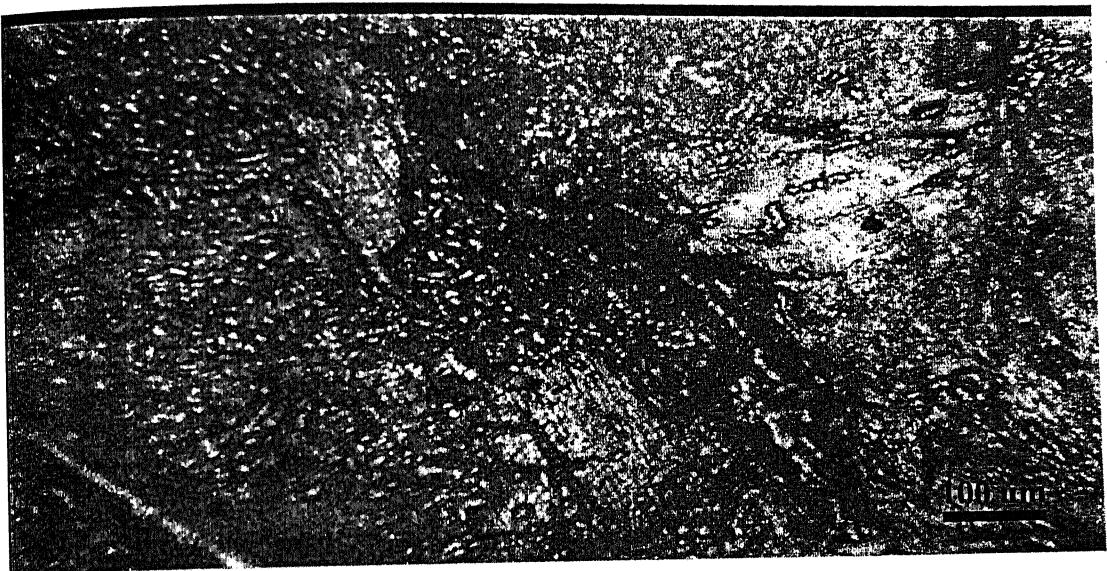


Fig. 4.44: Optical micrograph of laboratory synthesized wash opaque 2 at nucleation temperature of 600°C (holding temperature 1 hr) and crystallization temperature of 850°C (holding temperature 1hr) at 100X magnification.

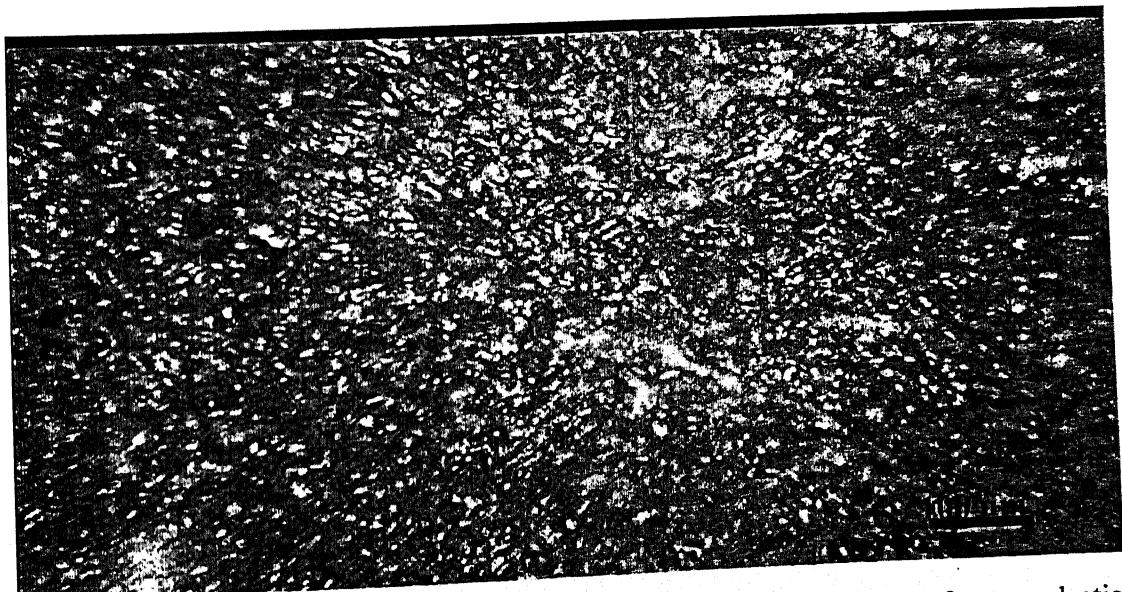
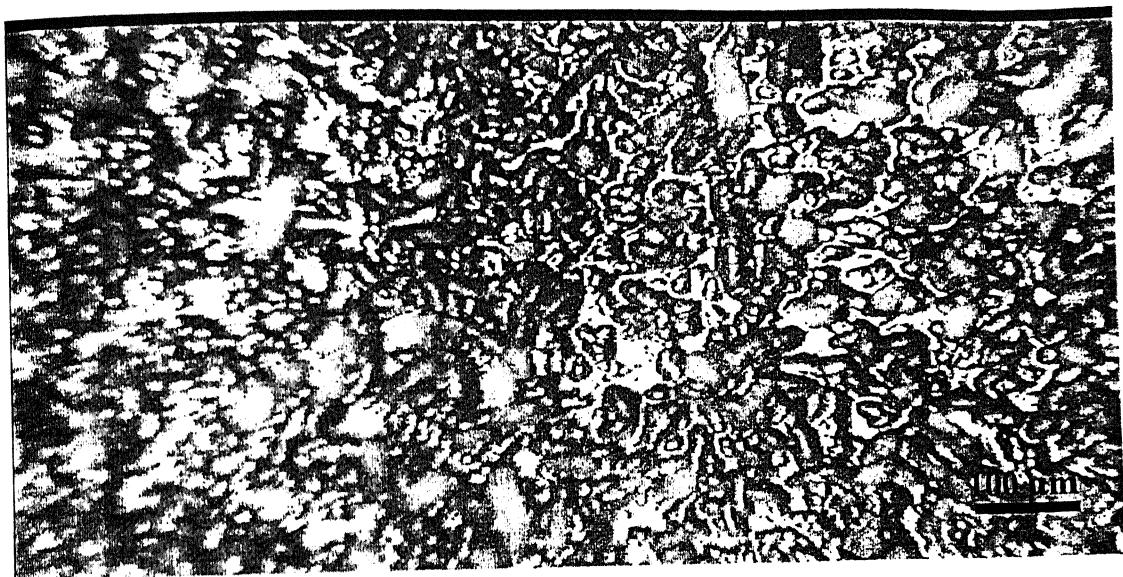
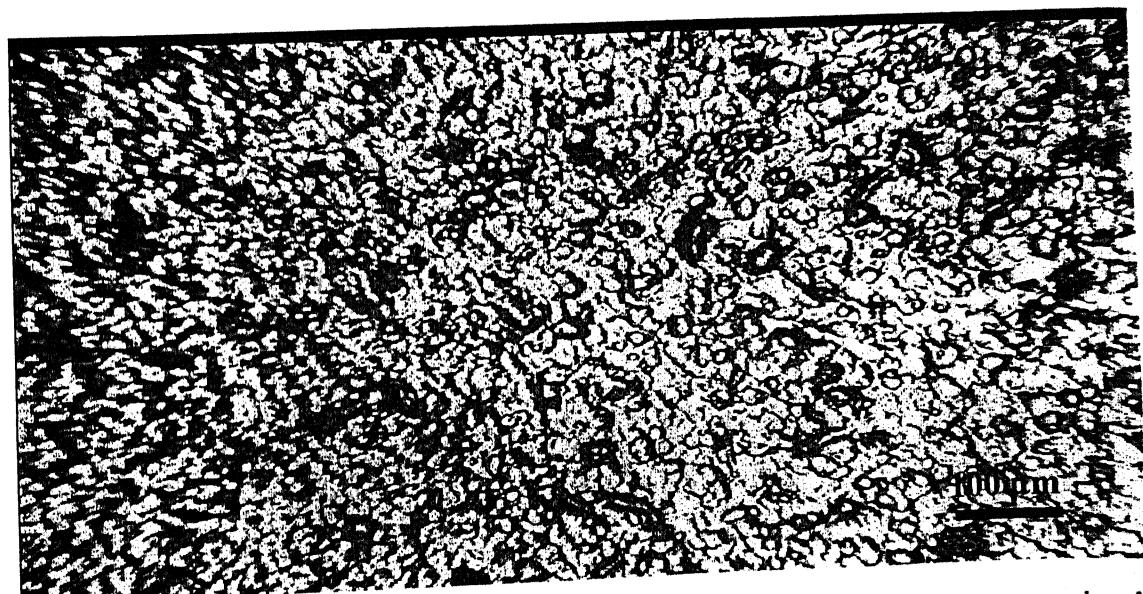


Fig. 4.45: Optical micrograph of laboratory synthesized wash opaque 2 at nucleation temperature of 600°C (holding temperature 1 hr) and crystallization temperature of 950°C (holding temperature 1hr) at 100X magnification.



**Fig. 4.46:** Optical micrograph of laboratory synthesized wash opaque 2 at nucleation temperature of 700°C (holding temperature 1 hr) at 100X magnification.



**Fig. 4.47:** Optical micrograph of laboratory synthesized wash opaque 2 at nucleation temperature of 700°C (holding temperature 1 hr) and crystallization temperature of 850°C (holding temperature 1hr) at 100X magnification.

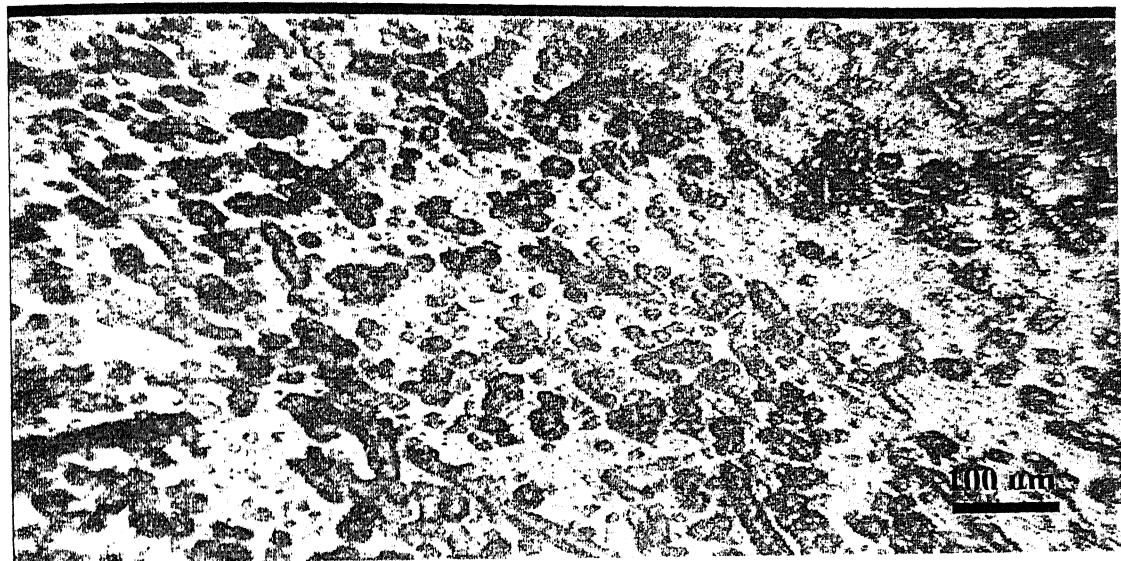


Fig. 4.48: Optical micrograph of laboratory synthesized wash opaque 2 at nucleation temperature of 700°C (holding temperature 1 hr) and crystallization temperature of 950°C (holding temperature 1hr) at 100X magnification.

#### 4.6 Hardness

The hardness values for as received dental alloy on Rockwell hardness tester are given in Table 4.8.

**Table 4.8:** Hardness values for as received dental alloy

No. of Trials	Hardness Values (Scale C)
Trial 1	20
Trial 2	20.5
Trial 3	21

## Chapter 5

### Discussions

#### 5.1 Composition

##### 5.1.1 Wash opaque

Compositional analysis results of the as received wash opaque suggest that this powder basically consists of a number of glass forming constituents.  $\text{SiO}_2$  is present as the major constituent followed by  $\text{Al}_2\text{O}_3$ . A fair amount of alkali such as  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$  and  $\text{CaO}$  is also present to lower the fusion temperature of the glass. The analysis also shows the presence of 12.58 wt % of  $\text{TiO}_2$ ,  $\text{SnO}_2$  and  $\text{ZrO}_2$ . US PATENT 4879136 has also mentioned the composition for wash opaque having very high percentage of these last three constituents (31 wt %). Presence of these constituents in wash opaque has special significance because they make the powder opaque so that it can mask the colour of metal substructure. As the literature suggests,  $\text{TiO}_2$  act as a nucleating agent as well in addition to having an opacifying effect.

The composition of laboratory synthesized wash opaque 1 was taken from US PATENT 4879136 whereas composition of wash opaque 2 was prepared by taking into consideration compositional analysis result for the as received wash opaque from NML, Jamshedpur and EDS results. However, some little changes have been made in the composition determined from NML, Jamshedpur and the composition actually taken for synthesis of the wash opaque 2. In the present case, 4 wt % of alumina has been replaced by 2 wt % of  $\text{B}_2\text{O}_3$  and 1 wt % each of  $\text{MgO}$  and  $\text{LiO}_2$  have been added. The reason for replacing alumina with boric oxide and alkalis was to lower the fusion temperature of glass without affecting its chemical stability. Alumina is second in importance to silica and combines with silica and basic fluxing oxides to prevent crystallization and give chemical stability to glass; however if too much alumina is present, it may not melt extensively enough and fusion may be incomplete. So, 2 to 3 wt % of  $\text{B}_2\text{O}_3$  was taken which not only improves the chemical stability by concentrating in the residual glass phase but also has lower melting range from 300-700°C. Since this oxide will lower the refractoriness of the glass phase if present in large amount, its wt % was limited to 2 to 3 wt %.  $\text{LiO}_2$  and  $\text{MgO}$  have been included to increase the alkali wt %.

### 5.1.2 Dentine and Enamel

The compositional analysis results of these powders from NML, Jamshedpur also indicate that these powders are glassy materials. In both the powders  $\text{SiO}_2$  is present as the major constituent. The basic difference between wash opaque and dentine is the presence of negligible or very small quantities of opacifying and nucleating agents such as  $\text{TiO}_2$ ,  $\text{SnO}_2$  or  $\text{ZrO}_2$  in the latter. In place of opacifying oxides, dentine consists of pigment and fluorescing oxides in the form of  $\text{Fe}_2\text{O}_3$  and  $\text{CeO}_2$  respectively. The presence of pigment and fluorescing oxide gives a special colour to this powder, which is used to match with the colour of natural teeth.

Both dentine and enamel are fairly similar in terms of the presence of nucleating agents. In enamel too these are present in very small quantities. US PATENT 5591030 has also given the compositions for dentine and enamel, which do not contain  $\text{TiO}_2$ ,  $\text{SnO}_2$  or  $\text{ZrO}_2$ . As discussed earlier, enamel is the outermost ceramic layer in a multilayered metal-ceramic restoration so it should contain pigments, which can give the same colour and fluorescence, which the natural teeth possess. At NML, Jamshedpur this pigment was identified as  $\text{ZrO}_2$ , which gives the white colour. However, analysis at NML, Jamshedpur could not give any fluorescing agent, which may be present in trace amount.

The composition for laboratory synthesized dentine 1 was taken from the US PATENT 5591030 with slight modification. Wt % of boric acid was reduced to 2 wt % and was replaced by 3.7 wt % of  $\text{CeO}_2$ . The reason for doing this replacement was to produce coloured glass so that its colour matches with the colour of as received dentine. The composition taken for laboratory synthesized dentine 2 was based on results obtained from NML, Jamshedpur and EDS results for as received dentine. In this composition also some minor modifications were done in the results obtained from NML, Jamshedpur. 2 wt % of alumina was replaced by same wt % of boric oxide to lower the fusion temperature of glass.

Laboratory synthesized enamel 1 composition was also taken from the US PATENT 5591030. The only modification was to reduce the wt% of boric oxide to 2 wt % and replace it with the pigment  $\text{ZrO}_2$  which produces white colour. Laboratory synthesized enamel 2 composition was based on the results obtained from NML, Jamshedpur and EDS results for as received enamel. The only change was to replace 3.47 wt % of alumina with

1 wt % of boric acid and 2.4677 wt % of  $ZrO_2$ . The wt % of  $ZrO_2$  was increased to produce desired colour.

### 5.1.3 Dental alloy

The compositional analysis result of as received dental alloy by EDS suggests that it is a Ni- Cr base alloy with Ni and Cr amounting to nearly 84.58 wt % of the total alloy. The remaining elements are Si, Mn, Fe, Nb and Mo, in smaller proportions.

## 5.2 XRD analysis

### 5.2.1 As received wash opaque, dentine and enamel

The XRD plots for the as received wash opaque, dentine and enamel have been given in Chapter 4. The XRD plots of wash opaque suggest that it is a crystalline material. So, combining compositional and XRD analysis results of wash opaque it can be said that it is not simply a glassy powder but a glass-ceramic material. The crystalline phase present in wash opaque was identified as Leucite ( $KAlSi_2O_6$ ) (cubic) by matching three high intensity peaks of wash opaque with standard JCPDS cards. Hence, heat treatment of laboratory synthesized glasses for wash opaque 1 and 2 was done at different nucleation and crystallization temperatures at a constant holding temperature of 1 hr in order to develop crystals of leucite. The nucleation and crystallization temperatures for heat treatment of wash opaque 1 and 2 were decided on the basis of results obtained from TG/DTA.

The XRD plots of the as received dentine and enamel suggest that these two are non-crystalline material because no sharp peaks were obtained. So, combining compositional and XRD analysis results it can be said that these two are simply coloured glass powders and not glass-ceramic like the wash opaque. Hence, further heat treatments of these powders were not done, as no crystalline phase was present in these powders.

### 5.2.2 As received dental alloy

The XRD plot for the as received dental alloy is given in Chapter 4. By matching the high intensity peaks of the dental alloy with standard JCPDS cards it was confirmed to be basically a Ni-base alloy. The elements present were identified as Ni, Cr, Si, Mn, Nb, Mo and Fe by EDS analysis.

### 5.2.3 Laboratory synthesized powders

#### 5.3.2.1 Laboratory synthesized wash opaque

The XRD plots for wash opaque 1 and 2 at different heat treatment temperatures are given in Chapter 4. Leucite ( $KAlSi_2O_6$ ) was found to be present as the main crystalline phase in all heat treatment processes, by matching the three high intensity peaks of their XRD plots with standard JCPDS cards. Thus, it can be said now that laboratory synthesized wash opaque 1 and 2 have converted from a glassy to a glass-ceramic material after heat treatment.

#### 5.3.2.2 Laboratory synthesized dentine and enamel

The XRD plots of laboratory synthesized dentine (1 & 2) and enamel (1 & 2) suggest that these are non-crystalline materials because no sharp peaks were present in their XRD plots. They are simply used as coloured glass powders.

### 5.3 Particle size analysis

The particle size analysis plots for the as received three ceramic powders & a dental alloy and laboratory synthesized dental ceramic powders are given in Chapter 4.

The particle size analysis plot for the as received wash opaque suggests that most of the particles lie in the range of 7.00 to 10.00  $\mu m$ . For dentine and enamel most of the particles are in the range of 4.00 to 7.00  $\mu m$ . So, the plot suggests that particles of wash opaque are coarser in comparison to dentine and enamel. As the literature suggests, particle size distribution of dental porcelain is critical in ensuring that the particles pack together as tightly as possible. So, dental porcelain powders should have wide range distribution of particle sizes such that smaller particles fill the spaces between the larger particles. The opaque layer is the first layer that is applied on metal-substructure followed by dentine and enamel layers. It is therefore necessary to maintain a sand paper consistency of the surface after firing the opaque layer. This type of surface helps in the adhesion of dentine and enamel layers on to the surface. Coarse powders can give rougher surface in comparison to fine powders having similar thermal stability. Therefore, opaque powder is coarser than dentine and enamel powders.

The particle size distribution plots for the laboratory synthesized wash opaque, dentine and enamel are given in chapter 4. The maximum particles for synthesized

opaque wash, dentine and enamel lie in the range of 4.00 to 7.00  $\mu\text{m}$ , which is rather close to the particle sizes of the as received powders.

#### 5.4 TG/DTA analysis

The TG/DTA curves for glass powders of laboratory synthesized wash opaque 1 and 2 are given in Chapter 4. The TG/DTA curve for wash opaque 1 suggests that the glass transition temperature is in the range of 370°C to 400°C and the crystallization temperature in the range of 1010°C to 1040°C. For wash opaque 2, the glass transition temperature is in the range of 350°C to 370°C and the crystallization temperature in the range of 950°C to 980°C. As the literature suggests the nucleation temperature of a glass-ceramic is 70°C to 100°C above glass transition temperature. Therefore, the nucleation temperatures for wash opaque 1 & 2 can be taken as 500°C, 600°C and 700°C and the crystallization temperatures as 750°C, 850°C, 950°C and 1050°C for wash opaque 1 and 750°C, 850°C and 950°C for wash opaque 2. The holding temperature was kept constant at nucleation and crystallization temperatures in all the cases. The purpose of choosing different nucleation and crystallization temperatures was to find the suitable percentage and size of leucite crystals in the microstructure so that an optimum condition could be found where the bond strength between the ceramic and metal could be the best.

#### 5.5 Optical microscopy

The optical micrographs of the wash opaque 1 and 2 at different nucleation and crystallization temperatures are given in Chapter 4. These optical micrographs show the presence of leucite crystals in a glassy matrix. This can be confirmed by the leaf type of structure of the crystals. Leafy structure is characteristics of leucite crystals.

For laboratory synthesized wash opaque 1 these micrographs show that as the temperature is increased the leucite percent and crystal size go on increasing upto 950°C irrespective of the nucleation temperature but beyond that temperature leucite percent goes on decreasing. This is clear from the optical micrographs obtained at 1050°C for different nucleation temperatures. For wash opaque 2, leucite percent and size go on increasing upto 850°C for all nucleation temperatures but after that leucite percent goes on decreasing. This is clear from the optical micrographs taken at 950°C. The reason for this trend is that as we go closer to crystallization temperature for glasses for final heat

treatment, crystals formed at lower temperatures may again dissolve into the glassy matrix.

The results of the present investigation have clearly shown that the laboratory synthesized powders of the wash opaque, dentine and enamel are quite comparable to the corresponding as received powders. The commercial exploitation of these powders will need many more experiments and trials over a long period of time.

## **Chapter 6**

### **Conclusions**

- 1) The as received wash opaque is a glass-ceramic material having leucite as the main crystalline phase present.
- 2) The as received dentine and enamel are simply coloured glassy powders and not glass-ceramics like the wash opaque.
- 3) A basic difference in the compositions of the as received wash opaque, dentine & enamel is that the wash opaque consists of high weight percent of nucleating and opacifying oxides such as  $TiO_2$ ,  $SnO_2$  or  $ZrO_2$  whereas dentine and enamel have negligible or very less wt % of these components.
- 4) The as received wash opaque particles are coarser than the as received dentine & enamel powders whereas dentine and enamel powders have nearly the same size distribution.
- 5) Laboratory synthesized wash opaque 1 & 2 are also glass ceramic materials having leucite as the main crystalline phase whereas laboratory synthesized dentine 1& 2 and enamel 1& 2 are coloured glassy powders.
- 6) As the final heat treatment temperature of wash opaque is chosen closer to the crystallization temperature the wt % of crystals goes on decreasing since crystals formed at lower temperature may again get dissolved in the glassy matrix.
- 7) The synthesized wash opaque, dentine and enamel powders have been found to have the characteristics similar to those of the corresponding as received powders.

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